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PUBLISHERS' NOTE

It is with regret that we announce the retirement of Professor P. E. WENGER as Editor of Analytica Chimica Acta. Professor WENGER was one of the founders of the journal and for fourteen years has rendered highly valuable service in his capacity as Editor. We are greatly indebted to him for his co-operation and devotion, and gladly take this opportunity to express to him our sincere thanks.

As from January 1, 1961, the duties of Editor will be shared by Professor PHILIP W. WEST, the former Regional Editor, and Dr. A. M. G. MACDONALD. To them we extend a cordial welcome and we trust that our association will be a long and fruitful one.

NOTE DE L'ÉDITEUR

Nous avons le regret d'annoncer la démission de Monsieur le Professeur P. E. WENGER comme Rédacteur de Analytica Chimica Acta. Le Professeur WENGER a été l'un des fondateurs de la revue et au cours de quatorze ans a rendu de précieux services en sa qualité de rédacteur. Les éditeurs lui sont redevables de sa coopération et de son dévouement; ils saisissent cette occasion pour lui exprimer leurs sincères remerciements.

A partir du 1er janvier 1961 la responsibilité de Rédacteur sera partagée entre le Professeur PHILIP W. WEST jusqu'à cette date "Regional Editor" et le Docteur A. M. G. MACDONALD. Nous leur souhaitons ici une cordiale bienvenue et nous sommes confiants que notre association sera longue et heureuse.

MITTEILUNG DES VERLEGERS

Mit Bedauern kündigen wir die Demission von Herrn Professor P. E. WENGER als Redakteur von Analytica Chimica Acta an. Professor WENGER war einer der Gründer der Zeitschrift und hat ihr im Laufe von vierzehn Jahren als Redakteur grosse Dienste erwiesen. Wir sind ihm für seine wertvolle Mitarbeit sehr verpflichtet und ergreifen gerne diese Gelegenheit um ihm unseren aufrichtigen Dank auszusprechen.

Ab 1. Januar 1961 wird die Verantwortung für die Schriftleitung von Professor PHILIP W. WEST, dem bisherigen "Regional Editor" und Dr. A. M. G. MACDONALD gemeinsam getragen werden. Wir heissen diese Mitarbeiter hier herzlichst willkommen und sind davon überzeugt, dass unsere Zusammenarbeit lang und ergebnisreich sein wird.

PHYSICAL PROCEDURES FOR THE ANALYSIS OF MIXTURES OF POLYCHLOROETHANES

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INTRODUCTION

A chlorination study required the analysis of mixtures of polychloroethanes. Such mixtures could contain seven constituents of similar chemical properties with relatively close boiling points. Most of the compounds exhibited a strong tendency to dehydrochlorinate and had to be stored in the absence of light. Variation in physical properties could be detected after several days. For this reason the compounds, which were prepared by classical methods, were given a number of water washes and fractionations immediately before use. Anhydrous magnesium sulphate was used for drying purposes.

Previous experience suggested that the analysis could be achieved by separation of the constituents into binary mixtures, with a minimum of thermal stress, followed by examination of such mixtures through refractive index measurements.

Separation into binary mixtures

The possible components of the polychloroethane mixtures were as follows (see Table I).

TABLE I

Components	*B.P. (760 mm)°C*
1,1-Dichloroethane	57
1,2-Dichloroethane	83.5
1,1,1-Trichloroethane	75
1,1,2-Trichloroethane	113
1,1,1,2-Tetrachloroethane	130
1,1,2,2-Tetrachloroethane	147
Pentachloroethane	92 (100 mm) (decomposes before boiling at 760 mm)

Fractionations of these mixtures using packed columns and reflux-ratio heads was discarded because of too much hold-up. A Vigreux column and sluice-head, with fine adjustment stop-cock, was substituted.

The technique of total reflux with intermittent take-off was rejected because of low recoveries (92%) due to thermal stress. Continuous fractionation gave similarly low recoveries and larger hold-up due to increased column length and higher reflux required. It did not establish satisfactorily the presence of small amounts (5%) of a

component where the study reaction-path was uncertain. Also, where recoveries and hold-up were controlled by shorter columns, sharpness of separation suffered. Discrepancies with test mixtures could be explained only by small amounts of ternary mixtures being produced near fraction turn-over points.

For these reasons, the two techniques were combined in the shorter column of the total reflux method. Continuous fractionation was used between possible component boiling points and total reflux with intermittent take-off, was used within ± 2–$3°$ of the boiling point. This increased recoveries to 98+% by lowering thermal stress and hold-up. It was also effective in increasing sharpness of separation at the critical points, without the penalty of lower recoveries obtained when the total reflux technique was used throughout the fractionation. The procedure established the reaction path.

Analysis of binary mixtures

Nine binary mixtures could be produced by the fractionation procedure from mixtures of the seven compounds resulting from the chlorination study. Within each binary mixture, the relationship of mass fraction and refractive index was found to be linear within the limits of refractive index measurement. The latter was considered to be 0.0002 with the Abbé type, refractometer held to $\pm$ 0.1°. This was equivalent to a composition variation within a binary mixture, of less than 0.5%. Such a mixture constituted only a fraction of the sample for analysis.

The net effect of these procedures gave accuracies between 0.5–2.0% on test mixtures; reproducibility tending to the lower figure and accuracy toward the higher.

The presence of hexachloroethane in the distillation residue was usually in the form of a solid solution in pentachloroethane. After weighing, further pentachloroethane was added to produce an homogeneous liquid phase of less than 20% hexachloroethane. The refractive index of this mixture established the hexachloroethane content of the *residue* and the pentachloroethane in same by difference.

Temperature dependence of refractive index

In association with the analytical work, the refractive indices were determined at intervals of 4° in the range 15–35°. It was found that parallel straight lines could be drawn, respectively, through points for each component, within the reproducibility of 0.0002.

From this it was found that for this series of compounds, $dn/dt = -5.26 \cdot 10^{-4}$, whereas the average general value[1] is $-4.5 \cdot 10^{-4}$, where the relationship is linear.

The values at 20° (see Table II) are in agreement with other workers (temperatures shown in brackets) and the above relationship.

TABLE II

Components	*Refractive index*
1,1-Dichloroethane	1.4164 (20°)[2]
1,2-Dichloroethane	1.4449 (20°)[3,4], (15°)[5] (25°)[6]
1,1,1-Trichloroethane	1.4379 (20°)[7]
1,1,2-Trichloroethane	1.4706 (20°)[2]
1,1,1,2-Tetrachloroethane	1.4828 (20°)[8]
1,1,2,2-Tetrachloroethane	1.4942 (20°)[9], (15°)[10]
Pentachloroethane	1.5030 (20°)[11], (15°)[10]
Hexachloroethane	1.5001 (30°) (20% in pentachloroethane)

SUMMARY

A mixture of seven polychloroethanes has been analysed by fractionation into binary mixtures using a combination of continuous fractionation and the technique of total reflux with intermittent take-off. The binary mixtures were analysed by refractive index measurements. The relationship between binary mixture refractive index and component mass fraction was found to be linear. The temperature dependence of the refractive indices of the polychloroethanes over the range, 15–35°, was also determined.

RÉSUMÉ

Des méthodes physiques sont proposées pour l'analyse de mélanges de polychloroéthanes, par fractionnement en mélanges binaires, et mesure des indices de réfraction de ces derniers.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Analyse eines Gemisches von Polychloräthanen durch Zerlegung (Destillation) in binäre Gemische und Messung deren Refraktionsindices.

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A RAPID METHOD FOR THE DETERMINATION OF AMMONIA (COMBINED) AND PHOSPHATE IN THE SYSTEM OF DIAMMONIUM PHOSPHATE AND DIPOTASSIUM PHOSPHATE

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INTRODUCTION

A simple titration method was required to determine phosphate and ammonium ions in the system $(NH_4)_2HPO_4$ and K_2HPO_4 which would be suitable for rapid routine control analysis without instrumental techniques.

When an excess of alkali is added to diammonium hydrogen phosphate, the ammonia can be quantitatively eliminated by boiling. Back titration of the excess alkali with $N/10$ hydrochloric acid followed by titration from $HPO_4^{-2} \rightarrow H_2PO_4^-$ yields titers which correspond to the ammonium and the phosphate. Methyl orange is the only indicator used. When dipotassium hydrogen phosphate is present, potassium can thus be calculated by difference.

EXPERIMENTAL PART

Standard solutions and reagents

Solution A. K_2HPO_4 aqueous solution containing 26.43 mg PO_4^{-3} per ml. *Solution B*. $(NH_4)_2HPO_4$ aqueous solution containing 12.47 mg NH_4^+ per ml and 33.02 mg PO_4^{-3} per ml. *Methyl orange* (*M.O.*) indicator, 0.05% aqueous. *Phenolphthalein* (*Ph*) indicator, 0.5% in 50% ethanol. *Mixed indicator* (*M.I.*) phenolphthalein + α-naphtholphthalein (2 parts 0.5% phenolphthalein in 50% ethanol and 1 part 0.1% α-naphtholphthalein in 50% ethanol[1]). *Brilliant yellow indicator paper* obtained by soaking strips of filter paper with a 0.1% brilliant yellow aqueous solution and drying.

The first stage of the procedure where phosphate and ammonium ions are determined by a single titration with phenolphthalein and methyl orange indicator, or mixed indicator and methyl orange indicator, is presented in Table I. Throughout experiments No. 1–3 a synthetic sample was obtained by mixing aliquots of solution A and solution B as given in Table I. The volume was brought to approximately 100 ml with carbon dioxide-free distilled water; standard carbon dioxide-free $N/10$ sodium hydroxide in the amounts stated in column 3 of Table I was added to the sample and the solution was boiled till free of ammonia. The solution was cooled and titrated first to phenolphthalein and subsequently to the methyl orange end-point. In experiment No. 2 the solution was half saturated with sodium chloride to repress hydrolysis[2]. In experiment No. 3 the mixed indicator was tested.

If the total theoretical alkalinity to methyl orange is calculated (column 6, Table I) we see that the total titer to methyl orange found is correct and reproducible (column 5, Table I), the maximum deviation being ± 0.75% relative.

TABLE I

THE DETERMINATION OF AMMONIUM AND PHOSPHATE BY A SINGLE TITRATION USING PHENOLPHTHALEIN AND METHYL ORANGE OR MIXED INDICATOR AND METHYL ORANGE

Experiment No.	Taken[a]		Added N/10 NaOH ($f = 1.034$)	Titrated		Theoretically required Total titer to M.O. N/10 HCl ($f=1.007$)	Found		Relative deviation	
	PO_4^{-3}	NH_4^+		Indicator	Actually titrated N/10 HCl ($f=1.007$)		PO_4^{-3}	NH_4^+	PO_4^{-3}	NH_4^+
	mg	mg	ml		ml	ml	mg	mg	%	%
	1	2	3	4	5	6	7	8	9	10
1			20.00	Ph	12.70					
				Ph → M.O.	7.35					
	59.45	12.47			20.05[b]	19.90[d]	70.31	14.25	+18.08	+14.28
2			20.00	Ph	12.40					
				Ph → M.O.	7.35					
	59.45	12.47			19.75[b]	19.90	70.31	14.79	+18.08	+18.61
3			20.00	M.I.	12.90 – 13.30[c]					
				M.I. → M.O.	7.05 – 6.65[c]					
	59.45	12.47			19.95[b]	19.90	67.44–63.60	13.87–13.15	+13.44 + 7.00	+11.23 + 5.45

[a] 1.00 ml of solution A plus 1.00 ml of solution B were taken in each experiment.

[b] Total titer to M.O.

[c] The end-point was not clearly distinguished.

[d] Calculation: 20.00 ml $N/10$ NaOH (column 3) corr. to 20.68 ml $N/10$ NaOH ($f = 1.000$). Alkali requirement for 12.47 mg NH_4^+ (column 2) corr. to 6.91 ml $N/10$ NaOH ($f = 1.000$). 13.77 ml $N/10$ NaOH ($f = 1.000$) corresponding to excess NaOH in the solution = 13.68 ml $N/10$ HCl ($f = 1.007$). 59.45 mg PO_4^{-3} (column 1) corresponds to 6.22 ml $N/10$ HCl ($f = 1.007$) ($HPO_4^- \rightarrow H_2PO_4^{-2}$). 19.90 is the theoretically required total back titer $N/10$ HCl ($f = 1.007$).

Representing the reaction schematically (Fig. 1) we see that if *ac* (compare columns 5 and 6 in Table I) is exact, the interpretation of the point *b* is not correct at the end-point of the phenolphthalein or mixed indicator (column 5, Table I). A displacement of *b* gives a displacement of *d* in the same direction. In our case it was displaced to the right giving too high results (by 5–18% relative) for phosphate as well as for ammonium ion (see columns 1, 2, 7, 8, Table I).

The second stage of the experimental part, therefore, involves the actual determination of point *b* by a direct titration of *bc*.

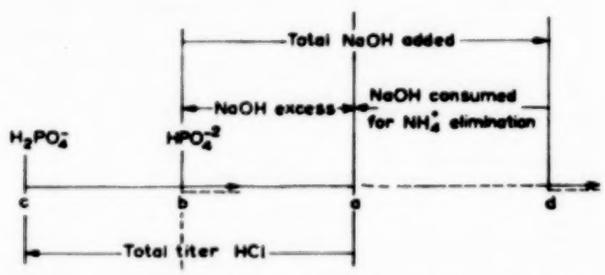

Fig. 1. Addition of NaOH (*bd*); elimination of NH_3 by boiling (*da*); back titration with HCl of excess NaOH to phenolphthalein or mixed indicator end-point (*ab*); titration $HPO_4^{-2} \rightarrow H_2PO_4^-$ from phenolphthalein or mixed indicator end-point to methyl orange (*bc*). Total titer HCl (*ac*). → displacement of *b* causes displacement of *d*.

DETERMINATION OF PHOSPHATE AND AMMONIUM BY TWO TITRATIONS USING METHYL ORANGE AS THE ONLY INDICATOR

When the sample is titrated directly with hydrochloric acid to methyl orange satisfactory values are obtained for $HPO_4^{-2} \rightarrow H_2PO_4^-$. If this titer is deducted from the total titer to methyl orange obtained in the first experimental part (column 5, Table I), the interference of the pH range of hydrolysis of the dibasic salt is avoided and stoichiometrically correct results are obtained.

Experiment No. 4

In this experiment an aliquot of the synthetic sample of $(NH_4)_2HPO_4$ and K_2HPO_4 (same composition as in experiments No. 1–3) was diluted to about 50 ml with distilled water and directly titrated with *N*/10 hydrochloric acid to methyl orange indicator. Amount of titrant used:

6.27 ml *N*/10 HCl ($f = 1.007$) to methyl orange = 59.98 mg PO_4^{-3}. This titer corresponds to *bc*, *i.e.* titration of $HPO_4^{-2} \rightarrow H_2PO_4^-$. The calculation of the NH_4^+ is therefore done in the following manner (see Fig. 2):

ac — *bc* = *ab* (excess NaOH in the solution)
db — *ab* = (total NaOH — excess NaOH) = *da* (corresponds to NH_4^+).

For example: In experiment No. 3 the total titer was 19.95 ml *N*/10 HCl ($f = 1.007$) (column 5, Table I).

19.95 ml (*ac*)	*Net titer*	
—6.27 ml (*bc*)	20.68 ml *N*/10 NaOH added (*db*)*	
13.68 ml *N*/10 HCl ($f = 1.007$) →	—13.77 ml *N*/10 NaOH excess (*ab*)*	
	6.91 ml (for NH_4^+)	(*da*)

$6.91 \cdot 1.804 = 12.47$ mg NH_4^+

* calculated to $f = 1.000$

TABLE II

VALUES OBTAINED BY THE PROPOSED VOLUMETRIC DETERMINATION OF AMMONIUM AND PHOSPHATE

Experiment No.	Taken			N/10 NaOH ($f = 1.004$) added to aliquot II	Found				Relative deviation	
	Composition of aliquots[a] I and II	Containing PO_4^{-3} mg	Containing NH_4^+ mg	ml	N/10 HCl ($f = 1.007$) Titration of aliquots I ml	II ml	PO_4^{-3}[b] mg	NH_4^+[b] mg	PO_4^{-3} %	NH_4^+ %
5	2.00 ml Solution A	52.86	nil	20.00	7.32	23.91	70.01	6.096	+0.92	−2.23
	0.50 ml Solution B	16.51	6.235							
	Total	69.37	6.235							
5a	As above			8.00	not done	12.00	N.D.[c]	6.01	—	−3.6
6	0.50 ml Solution A	13.22	nil	25.00	8.32	19.51	79.58	24.96	+0.4	+0.08
	2.00 ml Solution B	66.04	24.94							
	Total	79.26	24.94							

[a] In accordance with Fig. 2.
[b] Calculated as in Experiment No. 4.
[c] N.D. = Not determined.

If the total titer of $N/10$ hydrochloric acid is taken from Expts. No. 1 and 2 (column 5, Table I) the results are respectively: 12.27 mg NH_4^+ and 12.82 mg NH_4^+ (relative deviation = —1.6%; +2.8%).

These and the following results indicate that it is possible to determine the phosphate and ammonium content by two separate titrations in two aliquots of the sample using only methyl orange indicator.

Schematically the two titrations can be represented as follows:

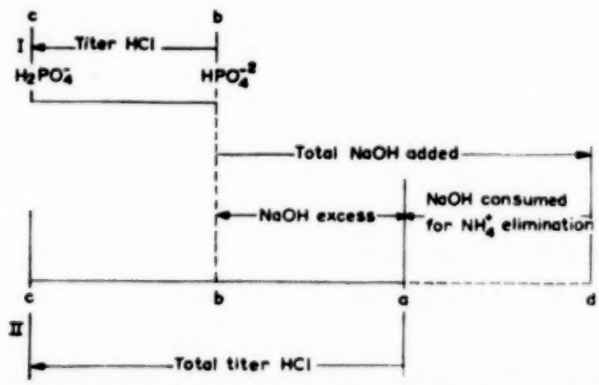

Fig. 2. Aliquot I. Direct titration with HCl to methyl orange end-point from HPO_4^{-2} to $H_2PO_4^-$ (*bc*). Aliquot II. Addition of NaOH (*bd*); elimination of NH_3 by boiling (*da*); back titration with HCl of excess NaOH + $HPO_4^{-2} \rightarrow H_2PO_4^-$ (*ac*).

From the above it follows that titers *ac* and *bc* were proved to be correct; it follows therefore that point *b* must be correct and consequently also *ab* as well as *ad* are reliable.

The reproducible values as obtainable by the method are shown in Expts. No. 5 and 6.

CONDITIONS OF DETERMINATION

Aliquot I (Fig. 2): The aliquot taken was diluted to about 50 ml with distilled water and titrated to methyl orange indicator with $N/10$ hydrochloric acid.

Aliquot II (Fig. 2): Another aliquot of the same composition was diluted to about 100 ml; $N/10$ sodium hydroxide was added and the solution boiled until free of ammonia; after cooling it was titrated to methyl orange indicator with $N/10$ hydrochloric acid.

Details and results are summarized in Table II. When diammonium hydrogen phosphate is titrated directly with $N/10$ hydrochloric acid to methyl orange (titer A ml) (first titration Fig. 2) the ammonium ion will require the presence of 2 A ml titer of $N/10$ sodium hydroxide, assuming that all the phosphate is present as the diammonium salt; then 2 A + 5 ml will be a sufficient excess to cover the total alkali requirement for the ammonia determination.

If the amount of the ammonium ion is known to be low the quantity of added alkali can be decreased. This is shown in experiment No. 5a (Table II).

METHOD

Procedure

1. Dilute an aliquot containing about 60 mg of phosphate with distilled water

to about 50 ml and titrate with $N/10$ hydrochloric acid to methyl orange (titer A).

2. Place another aliquot containing about 15 mg of ammonium ion in a 250-ml Erlenmeyer flask, add $N/10$ sodium hydroxide* in an excess of at least 5 ml, dilute to about 100 ml and boil till ammonia-free (about 15 min) testing the vapours with moist brilliant yellow paper. When the paper remains yellow no more free NH_3 is present in the solution. Cool and titrate with $N/10$ hydrochloric acid to methyl orange (titer B).

Calculation

1. Phosphate

$$\frac{\text{titer } A \cdot f(N/10\ \text{HCl}) \cdot 0.0095 \cdot 1000}{\text{aliquot ml}} = PO_4^{-3} \text{ in g/l}$$

2. Ammonium

$$\frac{\text{ml } N/10\ \text{NaOH corresponding to } NH_4^+ \cdot 0.001804 \cdot 1000}{\text{aliquot ml}} = NH_4^+ \text{ in g/l}$$

titer B — titer A = ml HCl corresponding to excess NaOH
Total $N/10$ NaOH added**— excess $N/10$ NaOH** = $N/10$ NaOH corresponding to NH_4^+.

Note

The calculation is made on the basis of identical aliquots.

ACKNOWLEDGEMENTS

Thanks are due to Dr. A. ALON, Chief Analyst, Mr. D. ELROI and Mrs. V. VARSANYI for their help and constructive criticism and the Management of Israel Mining Industries for the kind permission to publish this work.

SUMMARY

In systems containing $(NH_4)_2HPO_4$ and K_2HPO_4, it is possible to determine ammonium and phosphate ions by titrating 2 aliquots using methyl orange as the only indicator. Potassium can be calculated by difference. About 20 min are required for a single analysis.

RÉSUMÉ

Une méthode volumétrique est proposée pour le dosage de l'ammonium et de l'anion phosphorique dans un mélange de phosphate diammonique et de phosphate dipotassique. La teneur en potassium est calculée par différence.

ZUSAMMENFASSUNG

Beschreibung einer volumetrischen Methode zur Bestimmung von Ammonium und Phosphat in einem Gemisch von Diammoniumphosphat und Dikaliumphosphat. Der Gehalt an Kalium wird durch Differenz berechnet.

REFERENCES

1 A. VOGEL, *Quantitative Inorganic Analysis*, 2nd ed., Longmans, 1951, pp. 54, 64, 65, 66.
2 I. M. KOLTHOFF AND E. B. SANDELL, *A Textbook of Quantitative Inorganic Analysis*, 3rd ed., MacMillan, 1952, p. 536.

* If the order of magnitude of NH_4^+ is unknown, add $2 \cdot A$ ml of $N/10$ NaOH + 5 ml excess.
** To be calculated to factor 1.000.

BESTIMMUNG SEHR KLEINER MENGEN KOHLENDIOXYDS UND DIE ANALYTISCHE ANWENDUNG DES VERFAHRENS

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Es wurden bisher zahlreiche titrimetrische Verfahren zur Bestimmung kleiner Mengen Kohlendioxyds ausgearbeitet, weiterentwickelt und hinsichtlich ihrer Zuverlässigkeit überprüft. Das Studium der in diesem Zusammenhang aufgeworfenen Probleme hat auch gegenwärtig nichts an Aktualität eingebüsst, was auch verständlich ist, wenn man bedenkt, dass die titrimetrische Verfahrenstechnik anderen Messmethoden gegenüber grosse Vorteile besitzt. Als gebräuchlichstes Reagenz der Kohlensäure wird $Ba(OH)_2$-Lösung gebraucht. Die nicht in Reaktion getretene $Ba(OH)_2$-Menge kann unter Anwendung eines entsprechenden Indikators, meistens ist dies Phenolphthalein, acidimetrisch gemessen werden. BELCHER, THOMPSON UND WEST[1] befassen sich in ihrer jüngst erschienenen Arbeit, unter Berücksichtigung der Feststellungen anderer Forscher, eingehend mit den Problemen dieser Messmethode und bringen ein Verfahren zur Kohlenstoffbestimmung organischer Substanzen in Vorschlag. Im Rahmen dieser Arbeit sollen unsere eigenen Erfahrungen, Methoden und Messergebnisse behandelt werden. Wir befassten uns mit folgenden Themen:

I. Bestimmung des chemisch gebundenen Kohlendioxyds[2].
II. Bestimmung des chemisch gebundenen, aber in Freiheit gesetzten Kohlendioxyds.
III. Bestimmung des Kohlenstoffgehaltes organischer Verbindungen.

Wir möchten vor der Behandlung dieser einzelnen Themen einige bedeutende Probleme verfahrenstechnischen Charakters herausheben und unsere diesbezüglichen Untersuchungsergebnisse kurz zusammenfassen. Es handelt sich um Fragen des Fernhaltens atmosphärischer Kohlensäure und der Anwendungsmöglichkeit von Phenolphthalein als Indikator.

Der störende Einfluss der atmosphärischen Kohlensäure kann auf verschiedene Weise behoben werden. Meistens wird ein kohlendioxydfreier Gasstrom angewendet, dessen Unbequemlichkeit aber beim Arbeiten bekannt ist. TINSLEY, TAYLOR UND MOORE[3] verwenden Petroläther als Schutzsubstanz. Unsere Untersuchungen[2] ergaben, dass Pentan besser als Petroläther, Propan und Butan enthaltendes Pentan aber besonders vorteilhaft angewendet werden kann. Die Vorzüge einer solchen Flüssigkeit ergeben sich erstens aus ihrer grossen Flüchtigkeit und zweitens aus der verhältnismässig hohen Dichte der gebildeten Dampfphase. Es war mit Recht zu erwarten, dass die Dämpfe die Luft und damit auch das Kohlendioxyd aus dem zur Anwendung gelangenden Absorptions- bzw. Titrierkolben rasch austreiben werden. Pentan löst

Kohlendioxyd in messbarer Menge nur dann, wenn ein verhältnismässig hoher Partialdruck des Gases aufrechterhalten wird. Ein mit CO_2 gesättigtes Pentan gibt infolge des oben Gesagten beim Stehen im offenen Gefäss das Kohlendioxyd sehr rasch an die Atmosphäre ab und kann vorteilhaft nicht nur in diesem Fall, sondern auch zum bequemen Fernhalten der Luft d.h. also besonders des oft unerwünschten Sauerstoffs herangezogen werden. Schmalhalsige Kolben und mit entsprechend verlängerten Hahnansatzkapillaren versehene Büretten (Abb. 2) sichern eine grosse Messgenauigkeit. Dies bezieht sich in erster Linie auf das Arbeiten mit 0.05 und 0.01 *N* $Ba(OH)_2$-Lösungen.

Zur Anwendung des Phenolphthaleins (pH = 8.3–10) als Indikator sollen einige kurze Bemerkungen gemacht werden. Es kann bei der Endpunktanzeige von Titrationen im Mikromassstab nur dann gute Dienste leisten, wenn die Kohlensäure der Atmosphäre, besonders aber die der Atemluft ferngehalten wird. Pentan eignet sich zu diesem Zweck besonders gut. Wenn eine 0.01 *N* HCl- oder Essigsäurelösung unter Anwendung von Phenolphthalein und auch Pentan mit 0.01 *N* NaOH-Lösung titriert wird, so erfolgt eine gut bemerkbare Entfärbung der im Endpunkt rosafarbenen Lösung erst nach 25 Sek. Ohne Pentan tritt dies bereits nach 1 Sek auf. Man sieht also, dass Pentan tatsächlich vorteilhaft angewendet werden kann. Untersuchungen ergaben, dass die Entfärbung der auch durch Pentan geschützten Lösungen nicht auf die Einwirkung der atmosphärischen Kohlensäure, sondern auf strukturelle Veränderungen des Phenolphthaleins zurückzuführen ist. Die Ursache dieses Verhaltens des Phenolphthaleins kann mit der bereits in schwach alkalischer Lösung stattfindenden Aufspaltung seiner Laktonbindung erklärt werden. Man muss diese langsam verlaufende Reaktion beim Titrieren von Basen unbedingt berücksichtigen und dementsprechend verfahren. Es ist zweckmässig, wenn zu Beginn der Titration nur 2 Tropfen Phenolphthalein-Lösung zugegeben werden. Der Rest, vorteilhaft noch 4 Tropfen, wird erst vor dem Endpunkt zugefügt.

I. BESTIMMUNG DES ANORGANISCH-CHEMISCH GEBUNDEN KOHLENDIOXYDS[2]

Die Versuche wurden unter Anwendung sorgfältig hergestellter und analytisch kontrollierter 0.1 *N* NaOH- und 0.1 *N* $KHCO_3$-Stammlösungen durchgeführt. Als Reagenz wandten wir eine 40 Vol. % Äthanol enthaltende 0.05 *N* $Ba(OH)_2$-Lösung an, u. zw. deshalb, um die Hydrolyse des $BaCO_3$ zurückzudrängen. Aus dem gleichen Grunde wurde der mit $Ba(OH)_2$ versetzten und durch Pentan geschützten Lösung auch $BaCl_2 \cdot 2H_2O$ zugefügt. Betreffs Einzelheiten verweisen wir auf die bereits erwähnte, unter Druck befindliche Arbeit.

II. BESTIMMUNG DES CHEMISCH GEBUNDENEN, ABER IN FREIHEIT GESETZTEN KOHLENDIOXYDS

Die genaue Bestimmung des in der Gasphase befindlichen Kohlendioxyds hängt in erster Linie von der Zuverlässigkeit des angewandten Absorptionsverfahrens ab. Das ist verständlich, wenn man bedenkt, dass das Bariumhydroxyd nicht direkt mit dem in Lösung befindlichen Kohlendioxyd, sondern mit dessen Hydrolysenprodukt, mit der Kohlensäure reagiert. Es ist bekannt, dass im System Kohlendioxyd–Wasser die Hauptmenge des Kohlendioxyds als CO_2 und nicht als H_2CO_3 vorliegt, und dass die Hydrolyse im Gegensatz zur Neutralisationsreaktion, wenn Lauge zugegeben wird,

langsam verläuft[6]. Die experimentelle Tatsache, wonach eine 28%-ige KOH-Lösung CO_2 mit maximaler Geschwindigkeit zu absorbieren vermag[7], beweist ebenfalls, dass zur quantitativen Bindung des Kohlendioxyds als Carbonat Zeit beansprucht wird. Bei der quantitativen Messung kleiner Kohlendioxydmengen nach dem $Ba(OH)_2$-Prinzip müssen demgemäss zwei wichtige Zeitfaktoren berücksichtigt werden. Erstens die Absorption, also der Übergang des CO_2 aus der Gas- in die Flüssigkeitsphase, und zweitens die Hydrolyse zu Kohlensäure. Die Anwendung eines kontinuierlichen Gasstromes kann aus diesem Grund unserer Meinung nach zu systematischen Fehlern führen. Dies bezieht sich besonders auf den Fall, wenn $Ba(OH)_2$ in wässerig-alkoholischer Lösung zur Anwendung gelangt.

Unter Berücksichtigung der erwähnten Vorbedingungen arbeiteten wir ein neues Messverfahren aus, das sowohl im Halbmikro-, als auch im Mikromassstab angewendet werden kann. Die Absorption des in der Gasphase befindlichen Kohlendioxyds erfolgt nicht im offenen System, d.h. unter Anwendung eines kontinuierlichen Gasstromes, sondern im geschlossenen. Die Überführung des Kohlendioxyds zur $Ba(OH)_2$-Lösung sicherten wir durch ein Druckgefälle zwischen Absorptionsgefäss und Aussenluft.

Beschreibung der Einrichtung

Auf Fig. 1 ist die von uns angewandte Einrichtung abgebildet. Der 250 ml fassende Rundkolben (A) wird als Absorptions- und Titriergefäss verwendet. Den Verschluss nach der Atmosphäre hin sichert der sorgfältig eingeschliffene gedrungene Glasstopfen und ein daran befindlicher Karlsruher Hahn (3). Der Hals des Kolbens ist knapp über dem Schliff kelchartig erweitert. Der Kolben (A) kann über den Hahn (3), den Dreiweghahn (2) und ein Nadelventil (1) mit der Wasserstrahlluftpumpe verbunden werden. Zur Kontrolle des Vakuums dient ein einfaches Hg-Manometer (F). Durch entsprechendes Einstellen des Hahns (3) kann Kolben (A) auch mit dem eiförmigen Kolben (B) verbunden werden. Die am unteren Ende pfeifenartig nach aufwärts gebogene dickwandige Kapillare des Kolbens (B) mündet über Glashahn (4) in ein

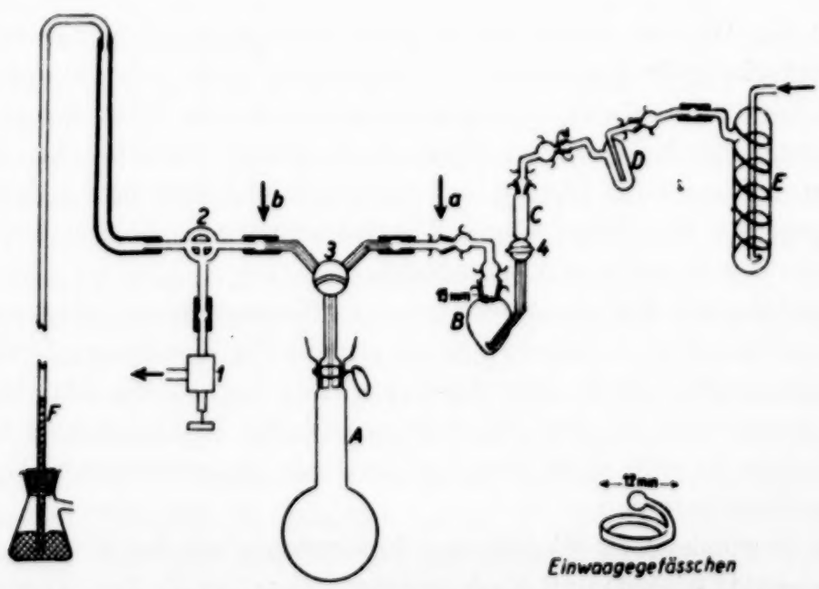

Fig. 1. A. Rundkolben zur Aufnahme der $Ba(OH)_2$-Lösung, B. Kolben zur Aufnahme der Untersuchungssubstanz, C. Trichterchen, D. Gaswaschgefäss, E. Gaswaschgefäss, F. Hg-Manometer, 1. Nadelventil, 2. Dreiweghahn, 3. Karlsruher Hahn, 4. Zweiweghahn.

10-ml Trichterchen (C). An letzteres sind die Gaswaschgefässe (D) und (E) angeschlossen u.zw. in der aus Fig. 1 ersichtlichen Anordnung. (E) ist ein Spiralgaswaschgefäss und dient zum Fernhalten der atmosphärischen Kohlensäure. Als Absorptionsmittel wurde etwa 28%-ige KOH-Lösung gewählt. Es ist sehr vorteilhaft, wenn Kolben (A), Dreiweghahn (2), Nadelventil (1) und Manometer (F) an ein Bunsen-Gestell befestigt werden. (Das Manometer kommt dabei auf die nach rückwärts geschwenkte Bodenplatte zu stehen). Ebenso verfährt man beim Befestigen der Geräteteile (B), (C), (D) und (E). Man erhält auf diese Weise zwei Geräte-Einheiten, die bequem auf der Tischplatte verschoben und mit Hilfe eines einzigen Glasschliffes (siehe Pfeil a auf Fig. 1) gasdicht verbunden werden können. Als Schmiermittel der Glasschliffe bewährte sich konzentrierte Schwefelsäure, noch besser aber dickflüssige Phosphorsäure.

Als Vorratsbürette wurde eine L. W. WINKLERsche[4] benutzt, deren Hahnansatzkapillare auf etwa 15 cm verlängert wurde. Die Vorratsbürette wurde mit niederschlagsfreier $Ba(OH)_2$-Lösung folgendermassen aufgefüllt (siehe Fig. 2a). Die Hahn-

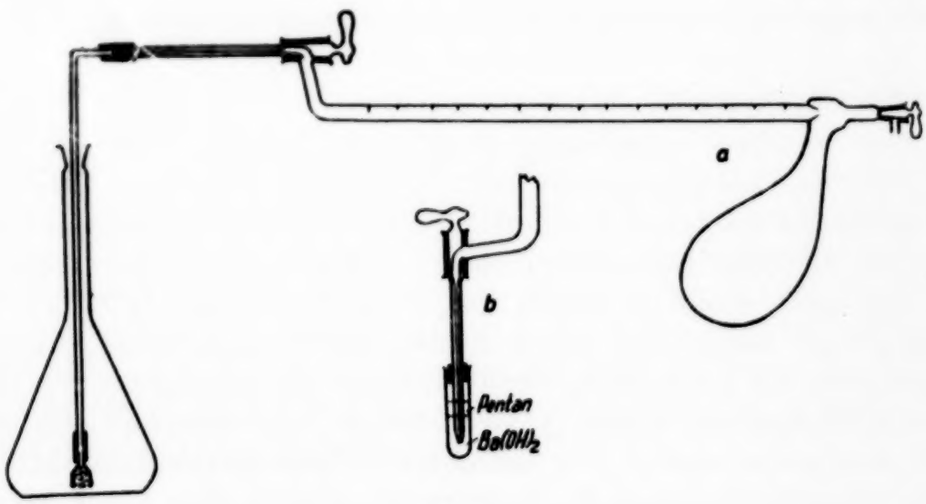

Fig. 2.

ansatzkapillare der Bürette wurde mit einer rechtwinklig gebogenen Glasröhre mit Hilfe eines Kautschukrohrstückchens, — an dessen Ende sich ein mit Baumwolle versehenes Trichterchen befand — angeschlossen und mit Hilfe der oben beschriebenen Vorrichtung mit Kohlendioxydfreier Luft gefüllt. Nun brachte man die Bürette in horizontale Lage (siehe Fig. 2a) und tauchte das Trichterchen in die vorbereitete und schon abgesetzte $Ba(OH)_2$-Lösung. Die Lösung wurde endlich in die Vorratsbürette mit Hilfe der Vorrichtung eingesaugt.

Um die Ausfällung von $BaCO_3$ an der Spitze der Hahnansatzkapillare zu vermeiden, wird diese, wie auf der Fig. 2b zu sehen ist, in ein mit der Masslösung beschicktes Probierrörchen eingetaucht. Die in dem Probierrörchen befindliche Masslösung ist mit einer Pentanschicht bedeckt, um das atmosphärische Kohlendioxyd fernzuhalten. Das Probierrörchen ist mit Hilfe eines an der Seite eingeschnitzten Korkes an der Hahnansatzkapillare befestigt.

Mit Hilfe der beschriebenen Einrichtung bestimmten wir den Kohlendioxydgehalt des Calciumcarbonats (Calcit) und Kaliumhydrogencarbonats. Das Kohlendioxyd des ersteren wurde mittels 60%-iger Perchlorsäure, das des letzteren aber unter Anwendung 85%-iger Schwefelsäure in Freiheit gesetzt und durch eine 0.1 *N* $Ba(OH)_2$-

Lösung absorbiert. Die zur Einwaage gelangenden Substanzen waren Calcitstücke, bzw. nach dem Verfahren von WINKLER hergestelltes Kaliumhydrogencarbonat. Die Einwaage erfolgte unter Benützung des auf Fig. 1 abgebildeten Gefässchens. Zum Fernhalten der atmosphärischen Kohlensäure (beim Einfüllen und Titrieren des Bariumhydroxyds) diente Pentan, als Indikator wurde Phenolphthalein angewandt. Leerversuche zeigten, dass erstens das Pentan und zweitens die 25–28%-ige KOH-Lösung die atmosphärische Kohlensäure vom System fernhält. Gleichfalls musste kontrolliert werden, ob 60%-ige Perchlorsäure (E. Merck) und 85%-ige Schwefelsäure als Lösungsmittel bzw. als Kohlendioxyd in Freiheit setzende Reagenzien verwendet werden konnten. Wir wollen bereits an dieser Stelle darauf hinweisen, dass beide Säuren (in der angegebenen Konzentration) nicht bloss den halbmikro-, sondern auch den mikroanalytischen Anforderungen entsprachen.

Beschreibung des Verfahrens im 0.1 N Massstab

In das Gaswaschgefäss (E) wird 25–28%-ige KOH-Lösung, in (D) 3–5 ml 60%-ige Perchlorsäure oder 85%-ige Schwefelsäure gefüllt und die Einrichtung gemäss Fig. 1 zusammengestellt. Hähne und Schliffe werden mit dickflüssiger Phosphorsäure gedichtet — der Glasstopfen des Kolbens (A) bleibt trocken! — und durch Gummiringe gesichert. Die Wasserstrahlluftpumpe wird nach Öffnen der Hähne (2, 3, 4) und Schliessen des Nadelventils (1) in Gang gesetzt. Durch entsprechendes Einstellen des letzteren (man beobachtet die in (E) aufsteigenden Luftblasen) kann das ganze System bequem durchspült werden. Das Gaswaschgefäss (D) wird in ein 50–60° warmes Wasserbad getaucht und auf diese Weise das in den konzentrierten Säuren gelöste Kohlendioxyd beschleunigt entfernt.

Inzwischen misst man die zu untersuchende Substanz, unter Anwendung des Gefässchens (siehe Fig. 1) und eines Uhrenglases als Unterlage, auf der Waage ab. Nadelventil (1) und Hahn (4) werden geschlossen und die Einrichtung beim Glasschliff (siehe Pfeil (a) auf Fig. 1) getrennt. Nach Entfernen des rechtwinkeligen Zwischenrohrstückes setzt man das Gefässchen mit Hilfe einer Pinzette auf den Boden bzw. auf die pfeifenartige Kapillarmündung des eiförmigen Kolbens (B). Die Geräteteile werden erneut aneinandergefügt und Hahn (4), sowie Nadelventil (1) geöffnet. Während des nun fortgesetzten Durchspülens nimmt man Kolben (A) ab, giesst in diesen etwa 10 ml Pentan, wartet kurze Zeit und füllt 10.00 ml 0.1 *N* $Ba(OH)_2$-Lösung ein. (Die verlängerte, etwa 10 cm lange Hahnansatzkapillare der Vorratsbürette soll tief unten am Hals des Kolbens anliegen). Der Kolben wird an seine ursprüngliche Stelle gebracht, durch entsprechendes Einstellen des Hahnes (3) mit der Wasserstrahlluftpumpe verbunden und nach weiterem Öffnen des Nadelventils (1) evakuiert. Die Grösse und Konstanz des Vakuums kann am Hg-Manometer (F) kontrolliert werden. Hahn (4) wird geschlossen und die konzentrierte Säure durch Umschwenken des Gefässes (D) in das Trichterchen (C) übergeführt. (Das Wasserbad wird von (D) nach (B) versetzt). Anschliessend verbindet man über Hahn (3) die Kolben (A und B), öffnet vorsichtig Hahn (4) und lässt die konzentrierte Säure aus (C) nach (B) fliessen. Die im Einwaagegefässchen befindliche Carbonat-Probe gerät mit der Säure in Berührung und löst sich darin unter CO_2-Entwicklung rasch auf. Bis zum gänzlichen Auflösen muss der durch Hahn (4) regulierte Luftstrom stark gedrosselt werden. Wenn auch bei ganz geöffnetem Hahn (4) keine Luftblasen mehr aufsteigen, wird Hahn (3) und Hahn (4) geschlossen, die Rohrverbindungen bei Pfeil (a und b) gelöst und der

Kolben (A) vom Gestell abgenommen. (Es ist vorteilhaft, wenn der Stopfen des Kolbens durch eine Gummischleife fixiert wird). Den Kolben stellt man auf 15–20 Min beiseite und schüttelt dessen Inhalt öfters durch. Anschliessend wird in die kelchartige Erweiterung etwa 10 ml Pentan gegossen und erst dann der Stopfen aus dem Glasschliff herausgehoben. Der im Kolben sich sofort bildende Pentandampf verhindert das Eindringen atmosphärischer Kohlensäure und gestattet ein äusserst bequemes Messen des überschüssigen Bariumhydroxyds. — Als Masslösung wird 0.1 *N* Salz- oder Perchlorsäurelösung, als Indikator 6 Tropfen 1%-ige Phenolphthaleinlösung angewandt.

1 ml 0.1 *N* $Ba(OH)_2$-Lösung entspricht 2.2005 mg CO_2 (log 0.34252)

TABELLE I

Substanz	*Einwaage* mg	*entspricht theoretisch* CO_2 mg	*Verbraucht* 0.1 *N* $Ba(OH)_2$-*Lösung* ml	*Gefunden* CO_2 mg	*Abweichung vom theoret. Wert* %
	21.8	9.61	4.38	9.63	+0.2
	27.9	12.28	5.56	12.24	−0.3
$CaCO_3$	14.6	6.42	2.94	6.46	+0.6
(Calcit)	19.4	8.53	3.85	8.47	−0.7
	28.0	12.32	5.57	12.27	−0.4
	18.1	7.96	3.62	7.92	+0.1
	18.1	7.95	3.61	7.94	−0.1
$KHCO_3$	24.6	10.81	4.89	10.77	−0.4
	31.1	13.67	6.24	13.75	+0.6

TABELLE II

DOLOMIT

Einwaage mg	CO_2-*Gehalt* g/g %
18.6	47.63
20.9	47.68
19.4	47.48
27.2	47.22
24.4	47.23
23.6	47.18
16.5	47.40

Die Messergebnisse sind in Tabelle I zusammengestellt. Es ist daraus zu ersehen, dass wir etwa 10 mg Kohlendioxyd mit einer Genauigkeit von ± 0.5% bestimmten, obzwar beide Substanzen, also das $CaCO_3$ und $KHCO_3$, bloss auf 0.1 mg genau abgewogen werden konnten. Unter Berücksichtigung dieses Umstandes muss das erhaltene Resultat als sehr zufriedenstellend bezeichnet werden. Die Analysenergebnisse einer Dolomit-Probe (siehe Tabelle II) bestätigen diese Feststellung ebenfalls.

Das beschriebene Verfahren konnte auch zur Bestimmung von etwa 1 mg CO_2 d.h. beim Arbeiten mit 0.01 *N* $Ba(OH)_2$-Lösung herangezogen werden. Als Untersuchungssubstanz diente Calcit. Da uns derzeit eine Mikrowaage nicht zur Verfügung stand, lösten wir das Problem der Einwaage folgendermassen. Sowohl das Calcit als auch das als Verdünnungssubstanz dienende Glas wurden im Achatmörser feinstens zerrieben, dann abgewogen und im gleichen Mörser vermengt. 10 mg Pulvergemisch enthielt 0.2283 mg $CaCO_3$.

Die 0.01 *N* $Ba(OH)_2$-Lösung wurde durch Verdünnung einer 0.1 *N* Lösung hergestellt und enthielt 50 g $BaCl_2 \cdot 2\,H_2O$ im L. Zweck dieses Zusatzes war die Hydrolyse des gebildeten $BaCO_3$ zurückzudrängen. Um noch eine grössere Wirkung zu erzielen, wurde dem nach der Absorption des Kohlendioxyds erhaltenen Reaktionsgemisch 5 ml 96%-iges Äthanol zugesetzt. Phenolphthalein bewährte sich in diesem Fall nicht als Indikator und musste durch α-Naphtolphthalein (pH = 7.0–9.0) ersetzt werden. Das Umschlagsintervall dieses Indikators liegt zwar, was das Titrieren bei Anwesenheit von $BaCO_3$ betrifft, etwas ungünstiger, — dieser Nachteil wird aber durch andere Vorteile ausgeglichen. Erstens dadurch, dass der Farbumschlag auch beim Arbeiten mit 0.01 *N* Masslösungen sehr genau festgestellt werden kann und zweitens, dass die Nähe des Endpunktes angezeigt wird. Der Umschlag erfolgt nämlich von blau über grün nach gelb. Das zur Anwendung gelangende Äthanol musste zwecks Entfernung des gelösten Kohlendioxyds zuerst ausgekocht und nach Abkühlung auf den erwähnten Indikator (eben gelb) eingestellt werden.

Beschreibung des Verfahrens im 0.01 N Massstab

Die Handhabung der Apparatur ist die gleiche wie beim Arbeiten im Halbmikromassstab, Kolben (A) wird nach erfolgter Absorption des Kohlendioxyds unter Anwendung von Pentan geöffnet und mit einer Pipette 5.0 ml 96%-iges Äthanol zugegeben. (Zur Vorbereitung und Aufbewahrung des Äthanols nimmt man am zweckmässigsten einen mit Glasschliff versehenen 100-ml Messkolben). Nach Zufügen von 2 Tropfen 0.2%-iger alkoholischer α-Naphtolphthaleinlösung titriert man mit 0.01 *N* HCl- oder $HClO_4$-Lösung bis zum Farbumschlag von grün nach gelb. Die zur Kohlendioxydbindung angewandte gleiche Menge 0.01 *N* $Ba(OH)_2$-Lösung wird unter Anwendung von 5 ml Alkohol ebenfalls titriert. Aus der Differenz der beiden Messungen kann der CO_2-Gehalt der Untersuchungssubstanz berechnet werden.

1 ml 0.01 *N* $Ba(OH)_2$-Lösung entspricht 0.2200 mg CO_2(log 0.34252)

TABELLE III

Einwaage		*Verbraucht*	*Gefunden*	*Abweichung*
Calcit-Glas-Pulvergemisch[a] *mg*	*entspricht theoretisch* CO_2 *mg*	*0.01 N* $Ba(OH)_2$-*Lösung ml*	CO_2 *mg*	*vom theoretischen Wert %*
75.7	0.760	3.43	0.754	—0.8
73.6	0.739	3.32	0.731	—1.1
73.6	0.739	3.38	0.744	+0.6
73.5	0.738	3.33	0.733	—0.65

[a] 10 mg Pulvergemisch enthielt 0.2283 mg $CaCO_3$.

Tabelle III enthält die Messergebnisse des Calcit–Glas-Pulvergemisches. Aus den Angaben der Tabelle ist zu ersehen, dass auf diesem Wege noch etwa 0.7 mg CO_2 gemessen werden können. Wenn berücksichtigt wird, dass erstens mit 0.01 *N* Masslösungen gearbeitet wurde und dass zweitens ein Pulvergemisch, also keine einheitliche Substanz zur Einwaage gelangte, so muss die Bestimmungsgenauigkeit von ±1% als sehr zufriedenstellend bezeichnet werden.

III. BESTIMMUNG DES KOHLENSTOFFGEHALTES ORGANISCHER VERBINDUNGEN

Das ausgearbeitete titrimetrische Verfahren konnte bei der organischen Mikroelemen-

taranalyse mit sehr gutem Erfolg an Stelle der üblichen gewichtsanalytischen Methode angewandt werden. Es wurde sowohl mit 0.1 *N* als auch mit 0.01 *N* Masslösungen gearbeitet. Im ersten Fall kam ein 250-ml, in zweiten ein 125-ml Rundkolben als Absorptions- und Titriergefäss zur Anwendung. Die Verbrennung erfolgte nach der Methode von KÖRBL[5]. Das Mikroverbrennungsrohr nach KÖRBL wurde (bei Pfeil (a) der Fig. 1) über einen Kapillarglashahn an den Rundkolben (A) mit Hilfe von Vakuumgummischläuchen (Glas an Glas) angeschlossen. Der Kapillarglashahn diente zur Regulierung des Gasstromes, also der durch das Vakuum angesaugten Verbrennungsprodukte. Die Versuche bewiesen, dass das zur Verfügung stehende Kolbenvolumen zur Aufnahme und Einspülung des gebildeten Kohlendioxyds vollkommen ausreicht. Die optimale Strömungsgeschwindigkeit betrug im 0.1 *N* Masstab (beim 250-ml Kolben) etwa 8 ml/Min, im 0.01 *N* Masstab (beim 125-ml Kolben) etwa 20 ml/Min. Die Silberpermanganatfüllung des Verbrennungsrohres wurde auf 440–450° gehalten. Die übliche Anordnung der Sauerstoffgaszuführung wurde beibehalten (Blasenzähler, Manostat usw.). Die Rückdiffusion des gebildeten Kohlendioxyds konnte durch einen in das Verbrennungsrohr eingeschobenen Glasstab verhindert werden. Wir wollen auch an dieser Stelle erwähnen, dass sich die Pentan-Methode als eine äusserst elegante, einfache und zuverlässige erwies. Das titrimetrische Verfahren unterscheidet sich in nichts von dem bereits beschriebenen. Eine genaue Beschreibung des Verfahrens soll auch schon aus diesem Grunde fortbleiben.

TABELLE IV

	Gravimetrisch nach Körbl			*Titrimetrisch (0.1 N Massstab)*	
	% H	*% C*	*Abweichung vom theoretischen Wert %*	*% C*	*Abweichung vom theoretischen Wert %*
	4.22	60.31	−0.9	61.03	+0.3
	4.34	60.59	−0.5	61.19	+0.5
	4.44	60.92	+0.1	60.86	0.0
	4.43	60.73	−0.2	60.77	−0.1
	4.33	60.64	−0.4	60.77	−0.1
	4.36	60.68	−0.3	61.03	+0.3
				60.53	−0.6
				60.96	+0.1
Mittelwert	4.35	60.64	−0.38	60.89	+0.05

Die Salicylsäure enthält theoretisch 4.38% H und 60.87% C.

Die Zuverlässigkeit und Genauigkeit des neuen Verfahrens wurde an Salicylsäure *p.a.* (Chinoin) als Untersuchungssubstanz geprüft. Tabelle IV enthält die mit der üblichen gewichtsanalytischen Methode, sowie die mit dem titrimetrischen Verfahren im 0.1 *N* Massstab erhaltenen Messergebnisse. Die Einwaage an Salicylsäure betrug in beiden Fällen 3–5 mg und erfolgte auf einer Sartorius Mikrowaage (Messgenauigkeit ±2 μg). Als Füllmittel der Absorptionsrohre diente Magnesiumperchlorat und Natronasbest. Aus den Angaben der Tabelle IV ist zu entnehmen, dass das titrimetrische Kohlendioxyd — bzw. Kohlenstoff-Bestimmungsverfahren zuverlässige und genaue Messergebnisse liefert. Die Genauigkeit des Verfahrens ändert sich kaum, wenn mit 0.01 *N* Masslösungen gearbeitet, d.h. bloss 0.8 mg Salicylsäure analysiert wird.

Tabelle V enthält unsere diesbezüglichen Messergebnisse. Wegen der Sicherung der Einwaagegenauigkeit mussten verhältnismässig grosse Salicylsäuremengen angegewandt werden, obwohl das titrimetrische Verfahren auch die C-Bestimmung von

TABELLE V

Titrimetrisch (0.01 N Masstab)	
% C	*Abweichung vom theoretischen Wert %*
60.88	0.0
60.59	—0.5
60.73	—0.2
60.88	0.0
60.75	—0.2
60.67	—0.3
60.52	—0.6
60.82	—0.1
60.75	—0.2
60.67	—0.3
Mittelwert 60.72	—0.24

Die Salicylsäure enthält theoretisch 60.87% C.

0.3 mg Substanz gestatten würde. Die vorzügliche Übereinstimmung des experimentell bestimmten und theoretisch berechneten Kohlenstoffgehalts beweist eindeutig, dass das Verfahren auch im Mikromasstab mit grosser Genauigkeit angewandt werden kann.

ZUSAMMENFASSUNG

Die Verfasser beschäftigen sich mit Problemen des Fernhaltens der atmosphärischen Kohlensäure, bzw. der Anwendungsmöglichkeit von Phenolphthalein als Indikator und bringen ein titrimetrisches CO_2-Bestimmungsverfahren in Vorschlag. Das chemisch gebundene oder in Freiheit gesetzte Kohlendioxyd wird durch überschüssige 0.1 oder 0.01 *N* $Ba(OH)_2$-Lösung gefällt bzw. absorbiert. Das Kohlendioxyd der Atmosphäre und Atemluft kann unter Anwendung von Pentan auf sehr einfache Weise ferngehalten werden. Im 0.1 *N* Masstab wird Phenolphthalein, im 0.01 *N* hingegen α-Naphtolphthalein als Indikator empfohlen. Das Verfahren kann mit sehr gutem Erfolg auch bei der organischen Mikroelementaranalyse angewandt werden.

SUMMARY

A volumetric method for the determination of very small quantities carbon dioxide is described. The procedure gives very satisfactory results and can be applied for the determination of carbon in organic compounds.

RÉSUMÉ

Les auteurs proposent une méthode volumétrique permettant le dosage de très petites quantités d'anhydride carbonique. Ce procédé donne des résultats très satisfaisants et peut être appliqué au dosage du carbone dans les substances organiques.

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THE ACCURATE DETERMINATION OF COBALT

II. GRAVIMETRIC METHODS AND IN PARTICULAR THE PHOSPHATE METHOD

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INTRODUCTION

Gravimetric methods used in the determination of cobalt have been critically discussed[1]. The precipitation of cobalt by α-nitroso-β-naphthol introduced by ILINSKI AND VON KNORRE[2] in 1885 was one of the first methods used for the determination of a metal with the aid of a selective organic reagent. In spite of its many defects, and the large number of other methods proposed, it remains, in modified form, one of the most frequently recommended methods for the determination of cobalt. No matter which modification is used, the method is open to much criticism. The precipitate itself is impure, due to the cobalt being in two valency states; the reagent also acts as an oxidant, itself becoming reduced to products which further contaminate the precipitate. Poisonous fumes are given off on heating, and the bulky nature of the precipitate and its tendency to stick to glassware make filtration difficult.

Ignition of the complex to the 'oxide' leads to further difficulty owing to its uncertain composition. Reduction of the 'oxide' by hydrogen to metallic cobalt for final weighing is the form of the method claimed to be most accurate. The important question here is whether the metallic residue contains traces of unreduced oxide. Also, in this form, weighing errors have the maximum effect. This, no doubt, is a reason why conversion of metallic cobalt to $CoSO_4$ for final weighing has also been recommended.

Reduction by hydrogen to the metal via "Co_3O_4" of uncertain composition has been recommended as the final procedure in many methods of cobalt analysis.

Variation in composition of the precipitate or final weighing form is the major source of error in a number of cobalt gravimetric methods *e.g.* the phenylthiohydantoic acid and cobaltinitrite methods. Its effect on the sulphate method will be apparent from the examination of $CoSO_4$ as a possible reference standard[1].

Slight solubility of the precipitate is the major source of error in other cobalt methods, particularly the phosphate method.

The aim of the present work was to examine experimentally a number of cobalt methods using a cobalt reference standard previously shown to be reliable[1]. In selecting methods for detailed examination, consideration was given to relevant data already available *e.g.* thermogravimetric behaviour of precipitates involved. Those

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finally chosen for critical examination were the anthranilate, phosphate, and electrolytic methods, the last being included for convenience with gravimetric methods. Methods depending on final reduction to metallic cobalt, or ignition as $CoSO_4$ were rejected for reasons given above.

REVIEW OF METHODS

The anthranilate method introduced by FUNK AND DITT[3] consists of adding excess of a 3% sodium anthranilate solution to a hot neutral or very slightly acid solution of cobalt.

$$2\ C_7H_6O_2NNa + CoCl_2 \rightarrow Co(C_7H_6O_2N)_2 + 2\ NaCl$$

The complex was dried at 105°–110°. GOTO[4] found the minimum pH for complete precipitation, and the maximum pH at which no precipitation took place to be 4.41 and 3.36 respectively. These values have been criticised and re-determined[5]. SHENNAN *et al.*[6] investigated the precipitation of cobalt anthranilate in buffered solution.

Although accurate results were claimed in unbuffered solution, low results were found in the presence of acetates and tartrates.

The phosphate method is analogous to the corresponding methods for zinc and magnesium, but although much investigated, it has not received similar recognition. The overall reaction may be represented by the equation

$$CoCl_2 + 2\ (NH_4)_2HPO_4 + H_2O \rightarrow CoNH_4PO_4 \cdot H_2O + NH_4H_2PO_4 + 2\ NH_4Cl$$

Ignition of the ammonium phosphate yields the pyrophosphate, an alternative weighing form.

$$2\ CoNH_4PO_4 \cdot H_2O \rightarrow Co_2P_2O_7 + 2\ NH_3 + 3\ H_2O$$

The corresponding method for magnesium has an extensive literature; a good account of the difficulties involved is given by KOLTHOFF AND SANDELL[7].

Earlier work on the cobalt method took no account of residual cobalt in the filtrate which DUFTY[8] and later SCHOELLER[9] determined gravimetrically following precipitation as sulphide. DUFTY's results, which indicated that there was a significant amount of cobalt in the filtrate, were ignored by some later workers. In assessing the phosphate method WILLARD AND HALL[10] invariably obtained high results.

More recently MATSUO[11] has investigated the effect of pH and ammonium ion concentration on the precipitation of cobalt ammonium phosphate. Precipitates produced under various conditions, were in each case ignited to the pyrophosphate and corrected for cobalt in solution, which was determined using α-nitroso-β-naphthol. Low results were obtained under all conditions, and the method was rejected.

The pyrolysis curve[12] for $CoNH_4PO_4 \cdot H_2O$ indicates that the pyrophosphate, which appears at 580°, is a good weighing form. Much of the work done on the phosphate method has been concerned with separating nickel from cobalt as well as a means of determining the latter.

Little attention has been given to the best method of producing a precipitate of satisfactory composition. The conflicting results of WILLARD AND HALL[10] and MATSUO[11] suggest variation in composition of the precipitate, although use of faulty reference standards may have been a contributory factor.

In its existing form, with the determination of cobalt in the filtrate by sulphide

precipitation followed by ignition to 'Co_3O_4', two gravimetric procedures are involved which detract considerably from the value of the method.

The electrolytic method has been recommended as the best for determinations involving large amounts of cobalt, and where high accuracy is desired. The method has been used to standardise cobalt stock solutions for use in assessing other methods of cobalt analysis. Electrolytic cobalt has been used by many workers as a reference standard.

Some of the unsatisfactory features are said to be: (*a*) incomplete deposition; (*b*) an occasional slight anode deposit in the absence of a reducing agent; (*c*) a contaminated deposit in the presence of a reducing agent; (*d*) a tendency for the platinum anode to dissolve during prolonged electrolysis.

The electrolytic method has been carried out with a greater diversity of procedure than any other method. Chemical composition of the electrolyte, time of electrolysis, current density, temperature, type of electrode, rate of stirring, and pH of the solution have been varied.

Various procedures have been evolved in an attempt to overcome the unsatisfactory features of the method. Treatment of the spent electrolyte with H_2S to determine residual cobalt via 'Co_3O_4' has been recommended[13]. KALLMAN[14] determined sulphur in the electrodeposited cobalt (arising from the use of sodium bisulphite), as $BaSO_4$, and corrected the weight of deposit accordingly.

EXAMINATION OF METHODS

The Anthranilate Method

Aliquots of a standard solution of cobalt were analysed using this method. Previous examination of filtrates from the anthranilate method had indicated the presence of small amounts of cobalt. All filtrates and washings, therefore, were made up to 500 ml and analysed for cobalt using a Nitroso-R-salt method. Generally, the filtrates were analysed as soon as possible because light turns sodium anthranilate brown. Otherwise the filtrates were stored overnight in a dark place.

Recoveries of cobalt in the Nitroso-R-salt method were shown to be unaffected by the amount of sodium anthranilate present. Some representative results are given in Table I.

In carrying out the above procedure, a drawback was encountered which previous

TABLE I

ANTHRANILATE METHOD

Normal procedure

No.	*Cobalt taken mg*	*Excess 3% anthranilate used %*	*Cobalt found as anthranilate mg*	*Filtrate cobalt mg*	*Total cobalt found mg*	*Error mg*
1	120.3	10	120.6	0.1	120.7	+0.4
2	120.3	15	120.5	0.2	120.7	+0.4
3	120.3	20	120.2	0.5	120.7	+0.4
4	120.3	30	120.3	0.2	120.5	+0.2
5	120.3	30	120.3	0.2	120.5	+0.2
6	120.3	30	120.5	0.1	120.6	+0.3
7	120.3	30	120.5	0.1	120.6	+0.3

Mean error: +0.31 mg +0.26%

workers do not appear to have mentioned. The precipitate is very light, and even on the most gentle boiling of the test solution spraying occurs, which results in particles of the precipitate being deposited on the walls of the beaker and the underside of the covering glass. Much care is required to remove this quantitatively.

In an attempt to overcome this difficulty, experiments were carried out to find whether heating the solution on a water bath could replace the five minutes' boiling. The results are shown in Table II.

TABLE II

ANTHRANILATE METHOD

Effect of heating on water bath rather than boiling

No.	*Cobalt taken mg*	*Excess 3% anthranilate used %*	*Time heated on bath min*	*Cobalt found as anthranilate mg*	*Filtrate cobalt mg*	*Total cobalt found mg*	*Error mg*
1	120.3	10	30	119.0	2.1	121.1	+0.8
2	120.3	15	30	120.1	1.1	121.2	+0.9
3	120.3	20	30	120.5	0.5	121.0	+0.7
4	120.3	30	30	120.5	0.3	120.8	+0.5
5	120.3	30	45	120.8	0.2	121.0	+0.7
6	120.3	40	45	121.2	0	121.2	+0.9
7	120.3	30	45	121.0	0.1	121.1	+0.8

Mean error: +0.76 mg +0.63%

In his determination of the pH range for complete precipitation, GOTO[4] used an acetate buffer. He did not detect the increased solubility of the precipitate in its presence, as SHENNAN, SMITH and WARD[6] did in later work.

Owing to the ease with which cobalt in solution may be determined using Nitroso-R-salt, some determinations were made in acetate and tartrate buffers. The method was similar to the first method described above. The results are given in Table III.

Nitrate ions are alleged to interfere with some cobalt methods. The anthranilate method was therefore carried out in the presence of 1 g potassium nitrate, but the filtrate cobalt was normal and the total cobalt unaffected.

TABLE III

ANTHRANILATE METHOD

Effect of acetate and tartrate

No.	*Cobalt taken mg*	*Excess 3% anthranilate used %*	*Buffer present*	*Cobalt found as anthranilate mg*	*Filtrate cobalt mg*	*Total cobalt found mg*	*Error mg*
1	120.3	30	3 g sodium acetate	118.4	0.2	118.6	—1.7
2	120.3	30	3 g sodium acetate	118.4	0.3	118.7	—1.6
3	120.3	30	3 g sodium tartrate	113.0	6.4	119.4	—0.9

*Experimental**

Reference standard: $[Co(NH_3)_5Cl]Cl_2$ was used. Stock solutions were prepared as described in Part I.

* General technique described in Part I (ref.[1]).

Sodium anthranilate solution: Batches of 5–8 g ordinary grade anthranilic acid were boiled with water in the presence of animal charcoal, filtered, and left to re-crystallise. The product after three treatments was very faintly yellowish, m.p. 144°. It was dried over P_2O_5.

Sodium anthranilate solution 3% was prepared in the following way. Slightly less than 7.5 g anthranilic acid was shaken up with 55 ml *N* NaOH diluted to 100 ml with water. One drop of phenolphthalein was added, and the solution made slightly acid by adding a saturated aqueous solution of anthranilic acid. The total volume was made up to 250 ml with water and the reagent stored in a dark bottle in a cool place.

Nitroso-R-salt solution: A 0.2% aqueous solution was prepared. It was found to be stable for several months if kept in a dark bottle and stored in a dark place.

Anthranilate method

The volume of the cobalt solution was adjusted to 200 ml, then 1.0 *N* sodium carbonate solution added until a slight cloudiness appeared. This was just cleared by addition of 1 : 200 (v/v) HCl. The solution was heated until it boiled, further additions of HCl being made to maintain a clear solution. An excess of 3% sodium anthranilate was slowly added, the solution being stirred. After five minutes of gentle boiling it was left to stand for one hour, filtered (X_4 sintered glass filter), and washed with cold 0.15% solution followed by 5 ml alcohol. After drying for one hour at 115° it was cooled and weighed.

Results and discussion

The anthranilate method is difficult to apply because there is a tendency for the precipitate to splash. The results are all slightly high, probably due to contamination of the precipitate by the reagent itself. When heating is carried out on a water bath, the error is doubled, thus making this procedure inadmissible.

If a factor were employed, it would have to be based on the total cobalt, including cobalt recovered from the filtrate, on account of the latter not being constant. From the results shown in Table I, such a factor would have the value 0.997.

The determinations made in the presence of sodium acetate and sodium tartrate indicate that the behaviour is not simply a question of solubility of the precipitate as previously suggested. In the presence of acetate ions, cobalt in the filtrate is normal, but the total cobalt is low. In contrast, the presence of tartrate ions leads to an abnormally high amount of cobalt in the filtrate, but a lower negative error for total cobalt. The method cannot be used in the presence of these ions even when residual cobalt is determined in the filtrate.

The anthranilate method is not entirely satisfactory. Its only advantage appears to be the non-interference by nitrate ion.

The Phosphate Method

The first procedure tried was based on the standard zinc method[15]. This consisted of adding an excess of 10% di-ammonium phosphate solution to a hot neutral cobalt solution buffered with a mixture of ammonium chloride and sodium acetate. The precipitate of cobalt ammonium phosphate was subsequently filtered, washed with 1% di-ammonium phosphate solution followed by alcohol, and ignited at 730° to the pyrophosphate for weighing. It was the phosphate method I used in Part I (ref. [1]).

Using $[Co(NH_3)_5Cl]Cl_2$ as reference standard, results were consistent but invariably high. The precipitate was rather fine, and easy to transfer, but had a tendency to make washing and filtering difficult by becoming tightly packed under suction.

In order to determine whether under different conditions of pH (*a*) the residual cobalt might be less or (*b*) the composition of the precipitate might be slightly different and give more accurate results, the pH values were adjusted before precipitation using 1.0 *N* NaOH or 1.0 *N* HCl, so that for the series the values were distributed between pH 6.0 and pH 8.5. The remaining procedure followed that of Phosphate method I.

After precipitation, the precipitate undergoes a series of colour changes, passing through a royal blue phase and ending in the violet form. It is essential for this sequence to be completed before filtration; in any of the intermediate forms the precipitate passes through the filter. In this series, the analyses at the higher pH values took about 3 h on the water bath to turn violet. The resulting loss of ammonia led to a large drop in pH, so that the final pH range for the series was narrow. The results indicated that the relative error was independent of pH for the procedure used.

MATSUO[11] in investigating the effect of pH on the precipitation of $CoNH_4PO_4 \cdot H_2O$ adjusted the pH after precipitation. This work, with slight modification, was repeated. The results are shown in Table IV.

TABLE IV

EFFECT OF pH ON THE PRECIPITATION OF COBALT AMMONIUM PHOSPHATE

Cobalt taken mg	*Cobalt found as $Co_2P_2O_7$ mg*	*Filtrate cobalt mg*	*Total cobalt mg*	*pH filtrate*
99.5	100.6	0.6	101.2	8.36
99.5	100.3	0.5	100.8	8.04
99.5	100.0	0.6	100.6	7.92
99.5	99.8	0.8	100.6	7.09
99.5	99.6	0.8	100.4	6.74
99.5	99.3	1.0	100.3	6.40
99.5	99.2	0.9	100.1	6.28
99.5	98.8	1.2	100.0	5.63

The alternative method of precipitating $CoNH_4PO_4 \cdot H_2O$ was then investigated. This consists of adding ammonia to an acid cobaltous solution containing di-ammonium phosphate. The method has been recommended by SCHOELLER[9] who determined soluble cobalt gravimetrically as sulphide and corrected the major fraction as $Co_2P_2O_7$ accordingly. SCHOELLER's method, with filtrate cobalt determined by Nitroso-R-salt was found to be very reproducible. A modification of it was used (Phosphate method II) in Part I. Results on the basis of $[Co(NH_3)_5Cl]Cl_2$ are included in Series II, Part I. The mean relative error was 0.19%. The precipitate in this form of the method is more difficult to handle. It has a tendency to stick to glassware.

It was found that if an equivalent amount of H_2SO_4 was used instead of HCl, the final results were lower by 0.1–0.2%. As the mean error using HCl was +0.19%, use of H_2SO_4 would produce almost exact results. A large number of determinations has confirmed this.

The only disadvantage found in using H_2SO_4 rather than HCl was that the change

from the blue amorphous precipitate formed initially, to the final violet form took twice as long (30–40 min).

Further investigation of this form of the phosphate method was carried out, the influence of the following factors being determined:

(*a*) excess of di-ammonium phosphate used; (*b*) excess of 1 : 1 ammonia added to effect precipitation; (*c*) time interval before filtration. A series of analyses using Phosphate method II was carried out, the precipitates being filtered 10 min, 20 min, 1 h, 4 h and 6 h after changing into the violet form; (*d*) effect of washing the precipitate with water rather than 1% di-ammonium phosphate solution; (*e*) effect of weighing as $CoNH_4PO_4 \cdot H_2O$ rather than $Co_2P_2O_7$. A series of determinations was carried out using Phosphate method II, in which the ammonium phosphate was weighed after drying at 100° and after ignition at 730°. The results are given in Table V.

TABLE V

PHOSPHATE METHOD

Effect of weighing as $CoNH_4PO_4 \cdot H_2O$ and $Co_2P_2O_7$

Cobalt found as $CoNH_4PO_4 \cdot H_2O$ (mg)	*Cobalt found as $Co_2P_2O_7$ (mg)*
148.1	147.4
147.8	147.6
77.6	77.3
77.5	77.2
77.4	77.2
77.2	77.1
77.3	77.0
102.9	106.0
106.2	106.1

Samples of $CoNH_4PO_4 \cdot H_2O$ produced by Phosphate method II were heated for 1 h at intervals of 5° above 100°, cooled and re-weighed.

A series of determinations using Phosphate method II was carried out in which the $CoNH_4PO_4 \cdot H_2O$ was ignited at various temperatures between 650° and 900°.

Experimental

Experimental details of the two principal phosphate methods (Phosphate methods I and II) have been given in Part I.

Reference standard: $[Co(NH_3)_5Cl]Cl_2$

Effect of pH on the precipitation of $CoNH_4PO_4 \cdot H_2O$. Sufficient NH_4Cl was added to the cobalt solution to give, together with 25 ml of 10% (w/v) di-ammonium phosphate solution added later, a 1 : 50 Co^{+2} : NH_4^+ molar ratio. The total volume was adjusted to 100 ml. After heating on a water bath for a few minutes, 25 ml di-ammonium phosphate solution, 10% (w/v), was added, and the pH adjusted using 1.0 *N* NH_4OH. The precipitate was left to stand overnight. It was filtered, washed with water followed by a little alcohol, dried at 100° and ignited to the pyrophosphate. The pH of each filtrate was measured and the residual cobalt determined using Nitroso-R-salt.

Effect of excess di-ammonium phosphate. The procedure was identical with Phosphate method II except that 10 ml 1 : 2 H_2SO_4 (v/v) was used instead of HCl, the precipitate

was washed with water instead of 1% (w/v) di-ammonium phosphate, and the amount of di-ammonium phosphate used (as 10% w/v solution) was that indicated in Table VI which contains the results.

TABLE VI

PHOSPHATE METHOD

Effect of excess di-ammonium phosphate

Cobalt taken mg	*Phosphate ion: Co^{+2} molar ratio*	*Total cobalt found mg*
99.4	2.5	99.4
99.4	4.3	99.4
99.4	10.0	99.6
99.4	25.0	99.9
99.4	50.0	100.3

Effect of adding different amounts of 1 : 1 ammonia. In Phosphate method II additional 1 : 1 ammonia was added so that the precipitate formed, just dissolved. The solution was stirred vigorously; the precipitate slowly appeared and the analysis continued.

Results and discussion

The results given for Phosphate methods I and II in Part I of this series indicate that variation in procedure leads to different results. This must be due to slight variations in the composition of the precipitates. Some of the published results in the literature using methods similar to Phosphate method I have claimed good results in contrast to the high results found in the present work. This may be due to a compensation of errors. For example, DICK[16] and KRAUS[17] use similar methods, but both neglect residual cobalt. In all the phosphate determinations, some residual cobalt was found in the filtrate, the amount varying from 0.4 mg to 3.0 mg for a total cobalt of 100 mg. Procedures based on acidimetric titration of $CoNH_4PO_4 \cdot H_2O$[18] would therefore lead to erroneous results. As the residual cobalt is not proportional to the total cobalt the use of a factor is not possible.

The results shown in Table IV support the trends shown in MATSUO's work[11], namely that the total cobalt is greater as the pH increases. However the actual values for total cobalt found, in relation to the amount taken, differs considerably, all the present results being high in contrast to those of MATSUO.

For example, at pH 8.0, for a NH_4^+: Co^{+2} molar ratio of 50 : 1 the result is 0.4% low whereas the present work indicates the total cobalt to be 1.4% high.

Washing the precipitate with water instead of 1% di-ammonium phosphate resulted in the amount of cobalt in the filtrate being increased by 50%. As the filtrate cobalt is determined in any case, there appears to be no advantage in using the ammonium phosphate.

Results on the basis of $CoNH_4PO_4 \cdot H_2O$ dried at 100° and then ignited at 730° are shown in Table V.

In all cases except one weighing as $CoNH_4PO_4 \cdot H_2O$ leads to high results. Heating the cobalt ammonium phosphate at increments of 5° above 100° produced erratic results. In the present work, 730° was used for ignition to the pyrophosphate. DUVAL's work[12] indicates that similar results could be expected over a wide range of temper-

ature. This was verified in a series ignited at various temperatures between 650° and 900°.

Table VI indicates that the final result in the Phosphate method is influenced by the quantity of di-ammonium phosphate added. Use of 10 ml of 10% di-ammonium phosphate represents a phosphate: cobalt molar ratio of 4.3. The results indicate that no appreciable error would result from a relatively large change in this ratio.

In determinations where just sufficient 1 : 1 ammonia had been added to dissolve the precipitate completely, the residual cobalt was much higher. As the Nitroso-R-salt method is only about 1% accurate, this procedure is liable to introduce a slight error, and could account for slightly less reproducible results being obtained.

A similar error is possible if the filtration is made too soon *e.g.* within 10 min of the precipitate having turned into the violet form. It was found that by filtering the hot solution over 10 mg cobalt was found in the filtrate. Furthermore, on cooling before making up to 500 ml for application of the Nitroso-R-salt procedure, there was a slight tendency for the $CoNH_4PO_4 \cdot H_2O$ to reprecipitate.

On the basis of the above work, the following procedure is recommended for the accurate determination of cobalt.

Recommended procedure

To the cobalt solution, which should be about neutral add 10 ml 1 : 2 H_2SO_4 (v/v), and 10 ml 10% (w/v) di-ammonium phosphate solution. Adjust the volume to 150 ml.

Heat until boiling and then transfer to a water bath; add sufficient 1 : 1 (v/v) ammonia to cause the precipitate formed to turn slightly purple and partly dissolve (approx. 25 ml required). Remove the beaker from the bath when the precipitate is violet and stand it in a cool place for at least one hour.

Filter through a X_4 sintered crucible, and wash with cold water followed by 5 ml 50% (v/v) alcohol. Dry the precipitate for 15 min at 100° and then ignite for one hour at 700°–800°. Cool and weigh as $Co_2P_2O_7$.

Dilute the filtrate and washings to 500 ml in a volumetric flask and transfer either a 10- or 25-ml aliquot to a beaker. Dilute to 40 ml, add one drop of phenolphthalein, and neutralise with 1 : 50 (v/v) HCl. Add a few ml excess of the acid, and boil gently on a hot plate. Add 4 ml 50% (w/v) sodium acetate solution, continue boiling, and then add 4 ml 0.2% (w/v) Nitroso-R-salt. Allow the colour to develop fully (about 2 min), add 2 ml conc. HNO_3 and boil for a further minute. Cool rapidly and make up to 100 ml. Treat a blank similarly. Measure the optical density using a 4-cm cell and a 545-mμ filter.

From a previously constructed calibration curve, determine the residual cobalt and add this to the cobalt found as pyrophosphate.

Table VII contains a typical series of results using the method.

TABLE VII

Cobalt taken mg	*Cobalt found* mg	*Relative error* %
241.0	240.9	0.0
241.0	241.3	+0.1
120.5	120.5	0.0
48.2	48.2	0.0
48.2	48.1	−0.2
24.2	24.2	0.0
24.2	24.2	0.0

The Electrolytic Method

The present work was mainly restricted to an examination and comparison of some existing procedures, and an assessment of electrolytic cobalt as a reference standard in the determination of cobalt.

After each test, the spent electrolyte and washings were examined for cobalt using Nitroso-R-salt. The usual assumption was made that all platinum lost from the anode would have been deposited on the cathode. Some representative results are given in Table VIII.

TABLE VIII

ELECTROLYTIC PROCEDURE UNDER VARIABLE CONDITIONS

No.	*Composition of electrolyte*	*Cobalt taken[a] mg*	*Time electrolysed min*	*Current density*	*Temp. of electrolyte °C*	*Change in wt. anode mg*	*Total cobalt found mg*	*Relative error %*
1	$CoSO_4$, NH_4Cl, NH_4OH, $NaHSO_3$	98.6	30	2A 3.25V	room	—0.5	99.9	+1.3
2	as in 1	99.0	45	2A 3.25V	room	—0.8	100.5	+1.5
3	as in 1 but without $NaHSO_3$	98.6	30	2A 3.25V	room	—0.9	98.9	+0.3
4	as in 3	98.6	30	2A 3.50V	room	—0.5	99.1	+0.5
5	$CoSO_4$, $(NH_4)_2 \cdot SO_4$, NH_4OH, Hydrazine SO_4	98.7	45	3A 2.25V	room	—0.3	100.1	+1.4
6	as in 5	98.7	120	1.5A	room	0	100.3	+1.6
7	as in 5	98.7	45	3A 2.25V	60	—1.6	100.1	+1.4
8	as in 5	98.7	45	3A 2.25V	75	—1.0	100.3	+1.3

[a] For this series, cobalt stock solutions were standardised using the phosphate method; in all electrolyses a high rate of stirring was maintained and the $NaHSO_3$ used was ordinary grade.

TABLE IX

ELECTRODEPOSITION FROM BICARBONATE–PEROXIDE COMPLEX

No.	*Cobalt[a] taken (mg)*	*Time electrolysed (min)*	*Current density*	*Change in wt. anode (mg)*	*Residual cobalt (mg)*	*Total cobalt found (mg)*	*Relative error %*
1	98.7	120	1.5A 3.5V	0	0.4	100.3	+1.6
2	96.2	65	2.0A 4.5V	+0.2	0.1	97.8	+1.6
3	96.2	60	2.0A 4.5V	—0.5	0.5	97.1	+0.9

[a] No. 1 was a sulphate solution; Nos. 2 and 3 were chloride solutions.

Attempts were made to deposit cobalt quantitatively from the bicarbonate–hydrogen peroxide complex. The results are given in Table IX.

The evidence suggesting that electrodeposited cobalt is contaminated is indirect. A typical electrolytic deposit was analysed by the phosphate method and shown to be impure.

In all the above work, the cathode deposit was weighed after drying at 100°. The effect of drying at higher temperatures indicated no change in weight up to 140°.

Experimental

Electrodeposition apparatus: A Griffin and Tatlock electrochemical analysis apparatus with provision for heating and stirring the electrolyte was used. Platinum gauze cylindrical electrodes were employed.

Reference standard: $[Co(NH_3)_5Cl]Cl_2$

General procedure. The solution, containing about 100 mg cobalt was electrolysed for a known time, a high rate of stirring being maintained. The average current passing and the potential difference between the electrodes was noted.

At the end of the electrolysis, the beaker was lowered from the electrode with the current still passing, the electrodes being washed with water at the same time. The spent electrolyte and washings were made up to 500 ml and cobalt was determined in an aliquot by means of Nitroso-R-salt. Blank tests carried out on the reagents other than cobalt indicated no interference with the method.

The washed electrodes were dipped into ethyl alcohol, dried at 100° for 15 min, cooled and weighed.

Deposition from the cobalt bicarbonate–peroxide complex. Sodium bicarbonate, 10 g and 10 ml 30% H_2O_2 were added to an aliquot of the cobalt solution. When effervescence had ceased, the sides of the beaker were washed down with water and the solution electrolysed in the manner described above.

Analysis of electrolytic cobalt. 50 ml of the cobalt solution was analysed using the Phosphate method II but nitric acid was used instead of sulphuric acid (because the subsequent cobalt deposit was dissolved in nitric acid, and nitrate ion affects the phosphate method giving low results). Another 50 ml of the cobalt solution was electrolysed in the presence of ammonia, ammonium sulphate and hydrazine sulphate. The weighed deposit was dissolved in nitric acid, and the solution analysed for cobalt using the same phosphate method with a correction for the amount of cobalt in the filtrate. The quantity of nitric acid used to dissolve the deposit was similar to that used in the first analysis.

Results and discussion

Table VIII contains representative results using slight variations of some recommended procedures for the determination of cobalt by electrodeposition. Results of electrolyses of the bicarbonate–peroxide complex are given in Table IX.

In all cases cobalt remained in the spent electrolyte at the end of the determinations and it ranged from 0.2 to 5.3 mg. The total cobalt in every case was invariably high, indicating that the deposit was contaminated. Excluding those containing no reducing agent, the results in Table VIII are 1.4% high.

Analysis of a typical deposit using the phosphate method gave the following results:

	Cobalt found
Analysis of 50 ml cobalt stock solution by phosphate method	98.7 mg
Weight deposit from 50 ml same solution	100.1 mg
Residual cobalt in spent electrode	0.3 mg
Deposit should therefore contain 98.4 mg cobalt (98.7 — 0.3)	
Cobalt actually found in deposit by phosphate analysis	98.6 mg

In this particular case the deposit contained about 1.6% impurity.

As to the nature of the contamination, sulphur is almost certainly one substance present; in the absence of sulphur the positive error is lower. Some previous investigations have suggested that carbon is one of the contaminants. Some electrodepositions were made in the absence of both sulphur and carbon, the electrolyte containing NH_4Cl, NH_4OH, and a little hydrazine hydrochloride. The results were still 0.7% high. It is difficult to avoid the conclusions that the deposit is contaminated with oxide or hydroxide.

A recent study of the electrodeposition of cobalt has been made by SALYER AND SWEET[19], who suggest, on the basis of another investigation[20], that the contamination might be due to the oxide, hydroxide, or water. The hypothesis is considered that below a cobalt concentration of about 0.005 *N* such compounds as $CoSO_4 \cdot 3Co(OH)_2 \cdot H_2O$ are deposited, although their experimental results do not support this theory in its simplest form. DELTOMBE AND POURBAIX[21] in a recent study of the equilibrium–pH study of the system $Co-H_2O$ have shown that in the absence of complexing substances, a deposit contaminated with oxide is possible above pH 6.3. Knowledge of the system $Co-NH_3-H_2O$ would be required to decide whether such contamination was possible in ammoniacal solution.

From the analytical standpoint, the results given by SALYER AND SWEET agree with the present work, the average error in their case being +2.2%.

In view of the contaminated deposits obtained using the various procedures, the electrolytic method is rejected for the accurate determination of cobalt.

CONCLUSIONS

Of the gravimetric methods examined for the accurate determination of cobalt, only a modification of the phosphate method is capable of giving accurate results. The electrolytic method gives very high results owing to a contaminated deposit.

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SUMMARY

Some gravimetric methods for determining cobalt have been examined in order to assess their value for the accurate determination of the metal. The electrolytic method was found to give high results (about 1.4%), and the anthranilate method slightly high results (0.2 – 0.3%). A modification of the phosphate method has been developed in which a former drawback, the solubility of $CoNH_4PO_4 \cdot H_2O$, has been overcome using a rapid spectrophotometric determination of residual cobalt. The final procedure developed has been found to give accurate results (±0.1 – 0.2%) and its use is recommended where this degree of accuracy is required.

RÉSUMÉ

Quelques méthodes de dosage gravimétrique du cobalt ont été examinées. La méthode au phosphate a donné les résultats les plus précis.

ZUSAMMENFASSUNG

Beschreibung einer kritischen Untersuchung über einige gravimetrische Methoden zur Bestimmung von Kobalt. Die besten Ergebnisse wurden mit einer modifizierten Phosphatmethode in Verbindung mit einer spektrophotometrischen Bestimmung erzielt.

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GRAVIMETRIC DETERMINATION OF MOLYBDENUM AND ITS SEPARATION FROM OTHER METALS WITH N-BENZOYLPHENYLHYDROXYLAMINE

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Some organic reagents have been used in the gravimetric determination of molybdenum[1-3], but the scope of application of these methods is limited. SHOME[4] has studied various derivatives of phenylhydroxylamine, with a view to improve on cupferron (ammonium salt of nitrosophenylhydroxylamine) which has several defects, and introduced N-benzoylphenylhydroxylamine as an analytical reagent for various metals[5]. SINHA AND SHOME[6] employed this reagent in the determination of nickel, cobalt, thorium and cerium. DAS AND SHOME[7] described a method for the colorimetric estimation of iron and copper using benzoylphenylhydroxylamine. Other investigators have found the reagent suitable in the gravimetric determination of tin[8], and niobium and tantalum[9-11], and also in the solvent extraction of thorium, lanthanum and uranium(VI)[12]. Recently SHOME and co-workers used the reagent to precipitate uranium, gallium, indium and the results will be published shortly. In the present work the reactions between benzoylphenylhydroxylamine and molybdenum(VI) ions were studied and a new method was developed for the gravimetric determination of molybdenum and for its separation from other metals. A preliminary report of this investigation[13] was published in 1957.

REACTIONS OF BENZOYLPHENYLHYDROXYLAMINE WITH MOLYBDENUM(VI) IONS

Benzoylphenylhydroxylamine formed a yellowish white precipitate with molybdenum(VI) ions. The precipitate was slightly soluble in hot water at or above 80°, in concentrated acids at lower temperatures, and in alcohol. Analysis of the pure molybdenum complex indicated its composition to be $MoO_2(C_{13}H_{10}O_2N)_2$. It decomposed at 165°–166°.

SOLUTIONS USED IN THE DETERMINATION OF THE METAL

A standard solution of ammonium molybdate was prepared to contain 3.08 mg of molybdenum per ml. Separate standard solutions of ferric alum, potassium chromate, copper sulphate, nickel sulphate, cobalt sulphate and sodium metavanadate were used in the study of the effect of foreign ions on the precipitation of molybdenum. A solution of benzoylphenylhydroxylamine in 95% ethyl alcohol was employed for the precipitation of molybdenum. All the chemicals employed were of A.R. quality.

DETERMINATION OF MOLYBDENUM(VI) BY IGNITING THE PRECIPITATE AND WEIGHING AS MOLYBDENUM TRIOXIDE

A known volume of the ammonium molybdate solution was diluted with distilled water, acidified with 10 *N* hydrochloric acid, and the alcoholic solution of benzoylphenylhydroxylamine (10–15 ml) was slowly added with constant stirring. The yellowish white precipitate of molybdenum appeared only slowly when the acid concentration was low. As the molybdenum complex was moderately soluble in alcohol, the final volume of the solution should not contain more than 5% of alcohol. The precipitate was stirred for about 15 min, allowed to settle for another 15 min, filtered and washed with 0.02 *N* hydrochloric acid solution. It was moistened with one or two drops of 6 *N* ammonium hydroxide solution to neutralise the free acid present, ignited at 500–525° and weighed as molybdenum trioxide.

TABLE I

DETERMINATION OF MOLYBDENUM(VI) BY WEIGHING AS MOLYBDENUM TRIOXIDE

Volume of solution = 300 ml

Mo taken g	*Temperature of solution* °C	*Benzoyl-phenyl-hydroxylamine* g	*Acidity of solution* N	*Weight of* MoO_3 g	*Mo found* g	*Error* g
0.0770	30	0.20	0.03	0.0675	0.0450	−0.0320
0.0770	30	0.30	0.03	0.1014	0.0676	−0.0094
0.0770	30	0.35	0.03	0.1140	0.0760	−0.0010
0.0770	30	0.42	0.03	0.1155	0.0770	0.0000
0.0770	30	0.42	0.01	0.1150	0.0767	−0.0003
0.0770	30	0.42	0.60	0.1152	0.0768	−0.0002
0.0770	30	0.42	1.60	0.1160	0.0773	+0.0003
0.0770	30	0.42	2.50	0.1159	0.0773	+0.0003
0.0770	50	0.42	0.03	0.1156	0.0771	+0.0001
0.0770	75	0.42	0.03	0.1158	0.0772	+0.0002
0.0770	80	0.42	0.03	0.1129	0.0753	−0.0017

The effects of various factors such as temperature of solution, reagent concentration and acidity of the reaction medium on the precipitation of molybdenum were studied. The results (Table I) indicate that the precipitation of molybdenum(VI) is complete when the supernatant liquid contains 0.03% (w/v) of the organic reagent in excess at a temperature below 70° and the acidity of the solution ranges from 0.01 to 2.50 *N* hydrochloric acid.

Molybdenum(VI) was also determined (Table II) in the presence of chromium(VI), vanadium(V), iron(III), cobalt(II), nickel(II), and copper(II). The metal was separated from cobalt, nickel or copper by precipitating molybdenum(VI) ions with benzoylphenylhydroxylamine (0.44 g) in the presence of a sufficient amount of acid, and washing the precipitate with 0.2 *N* hydrochloric acid, followed by a 0.02 *N* solution of the same acid. In the other separations the precipitate was washed with 0.02 *N* hydrochloric acid only. The interference of iron(III) and vanadium(V) ions was masked by adding disodium ethylenediamine tetraacetate (1–2 g) which forms stable complexes with the two metal ions. When the vanadate was heated with EDTA, it was probably reduced to vanadyl ion before the complex formation[14].

TABLE II

DETERMINATION OF MOLYBDENUM(VI) BY WEIGHING AS MOLYBDENUM TRIOXIDE

Volume of solution = 300 ml

Mo taken g	*Foreign ion added* g	*10 N HCl added* ml	*Weight of MoO_3* g	*Mo found* g	*Error* g
0.0770	0.128(Cu^{+2})	10.0	0.1160	0.0773	+0.0003
0.0770	0.200(Ni^{+2})	10.0	0.1161	0.0774	+0.0004
0.0770	0.107(Co^{+2})	10.0	0.1152	0.0768	—0.0002
0.0770	0.004(Cr^{+6})	1.0	0.1158	0.0772	+0.0002
0.0770	0.009(Cr^{+6})	1.0	0.1160	0.0773	+0.0003
0.0770	0.056(Fe^{+3})	0.3	0.1165	0.0777	+0.0007
0.0770	0.112(Fe^{+3})	0.4	0.1163	0.0775	+0.0005
0.0770	0.003(V^{+5})	0.8	0.1163	0.0775	+0.0005
0.0770	0.005(V^{+5})	1.0	0.1165	0.0777	+0.0007

DETERMINATION OF MOLYBDENUM(VI) BY WEIGHING THE METAL COMPLEX DIRECTLY

An aliquot (10–25 ml) of the ammonium molybdate solution was diluted with distilled water, acidified with 10 *N* hydrochloric acid, heated to about 60° and molybdenum was precipitated by adding a solution of benzoylphenylhydroxylamine (0.25–0.44 g) in alcohol (10–15 ml). The molybdenum precipitate was heated at 60° for 30 min on a water-bath, filtered on a No. 3 glass-sintered crucible, washed with warm (60°) 0.02 *N* hydrochloric acid and finally with 10 ml of distilled water. The precipitate was dried at 110–115° for one hour and weighed. The molybdenum content was calculated on the basis that the precipitate contained 17.37% of the metal.

Molybdenum was also precipitated in the presence of other metallic ions as described before, but the precipitation and washings were carried out under warm conditions to prevent the contamination of the molybdenum complex with the precipitant.

TABLE III

DETERMINATION OF MOLYBDENUM(VI) BY WEIGHING THE PRECIPITATE DIRECTLY

Volume of solution = 300 ml

Mo taken g	*Foreign ion added* g	*10 N HCl added* ml	*Disodium EDTA added* g	*Weight of ppt.* g	*Mo found* g	*Error* g
0.03080	—	1.0	—	0.1777	0.03086	+0.00006
0.07700	—	1.0	—	0.4431	0.07695	—0.00005
0.03080	0.154(Ni^{+2})	6.0	—	0.1769	0.03072	—0.00008
0.03080	0.107(Co^{+2})	6.0	—	0.1780	0.03091	+0.00011
0.03080	0.051(Cu^{+2})	6.0	—	0.1781	0.03092	+0.00012
0.03080	0.124(Cu^{+2})	6.0	—	0.1767	0.03068	—0.00012
0.04620	0.384(Fe^{+3})	0.4	3.0	0.2638	0.04581	—0.00039
0.04620	0.772(Fe^{+3})	0.4	6.0	0.2641	0.04586	—0.00034
0.03080	0.004(V^{+5})	0.8	2.0	0.1763	0.03061	—0.00019
0.03080	0.008(V^{+5})	0.8	3.0	0.1758	0.03053	—0.00027

It can be seen from the results given in Table III that molybdenum(VI) can be determined by weighing as $MoO_2(C_{13}H_{10}O_2N)_2$ and this offers a simple method for the

separation of molybdenum from many other metal ions. Since chromium(VI) has a tendency to oxidise benzoylphenylhydroxylamine, especially in presence of hot acid, molybdenum(VI) cannot be determined in the presence of chromium(VI) by weighing the complex directly. Benzoylphenylhydroxylamine precipitates tungsten(VI) in acid medium, and it is not possible to separate molybdate from tungstate with the reagent.

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One of the authors (S. K. SINHA) is indebted to the Ministry of Scientific Research and Cultural Affairs, Government of India, for the grant of a scholarship.

SUMMARY

N-Benzoylphenylhydroxylamine is employed as a precipitant for the determination of molybdenum(VI). The precipitate can be weighed either directly or as molybdenum trioxide after ignition. Molybdenum can be determined in the presence of appreciable amounts of iron(III), cobalt(II), copper(II), chromium(VI) and vanadium(V).

RÉSUMÉ

La N-benzoylphénylhydroxylamine est proposée comme réactif pour le dosage gravimétrique du molybdène(VI). Ce dosage peut s'effectuer en présence de fer(III), de cobalt, de cuivre, de chrome-(VI) et de vanadium.

ZUSAMMENFASSUNG

Zur gravimetrischen Bestimmung von Molybdän(VI) neben Eisen(III), Kobalt, Kupfer, Chrom(VI) und Vanadium kann N-Benzoylphenylhydroxylamin verwendet werden.

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GRAVIMETRIC DETERMINATION OF BERYLLIUM WITH N-BENZOYLPHENYLHYDROXYLAMINE

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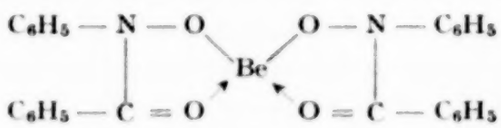
N-Benzoylphenylhydroxylamine has been recommended as a precipitant in the quantitative analysis of several metals by various authors[1]. In the present investigation, it is employed in the gravimetric estimation of beryllium.

Stable complexes of beryllium are known to be formed with chelating agents which have oxygen as the electron donors. Benzoylphenylhydroxylamine provides such a favourable grouping and forms with beryllium a complex of composition $Be(C_{13}H_{10}O_2N)_2$. The complex is best represented as a chelate:



Since the precipitation of iron or aluminium with benzoylphenylhydroxylamine is complete at pH 4.0 whereas the precipitation of beryllium starts at pH 4.6, it is possible to precipitate iron or/and aluminium while beryllium remains in solution by a proper control of pH before adding the precipitant. Benzoylphenylhydroxylamine may also be used for precipitating titanium in the presence of beryllium at pH 1. Beryllium can be subsequently precipitated with the reagent after raising the pH of the filtrate. The precipitate may be either ignited to form beryllium oxide or weighed as $Be(C_{13}H_{10}O_2N)_2$.

SOLUTIONS USED IN THE DETERMINATION OF THE METAL

Standard beryllium solution

Beryllium hydroxide was precipitated from a solution of beryllium nitrate in presence of the disodium salt of ethylenediamine tetraacetic acid, washed with water, dissolved in nitric acid and diluted. The beryllium content of the solution was determined by the oxide method.

Foreign ions

Solutions of ferric nitrate, aluminium nitrate and titanium sulphate were employed when beryllium was precipitated in the presence of these metal ions.

Benzoylphenylhydroxylamine solution

A solution of the reagent in 95% ethyl alcohol was used for the precipitation of beryllium.

All the chemicals used were of A.R. quality.

PROPERTIES AND COMPOSITION OF THE BERYLLIUM COMPLEX

The beryllium complex of benzoylphenylhydroxylamine was obtained in the form of a white granular substance, insoluble in water up to a temperature of 70° and easily soluble in chloroform. The solubilities of the complex in carbon tetrachloride, acetone and 50% ethyl alcohol were comparatively low. It decomposed when treated with moderately concentrated mineral acids and melted with decomposition when heated to 220°. The pure complex was analysed for beryllium and nitrogen and the results indicated its composition as $Be(C_{13}H_{10}O_2N)_2$.

	Experimental, %	*Theoretical, %*
Be	2.06	2.08
N	6.41	6.46

DETERMINATION OF BERYLLIUM

A known quantity of the beryllium solution was diluted to 200 ml with distilled water, heated to 50–60° and the solution of benzoylphenylhydroxylamine (0.2–0.3 g in 10 ml of alcohol) was added slowly with constant stirring. Ammonium hydroxide (3 *N*) was then gradually added to adjust the pH of the solution to between 5.5 and 6.5. The precipitate was allowed to stand for a few minutes, filtered, washed and ignited to the oxide. The results recorded in Table I indicate that beryllium is quantitatively precipitated from aqueous solution by adding benzoylphenylhydroxylamine and can be determined by igniting the precipitate to beryllium oxide.

TABLE I

DETERMINATION OF BERYLLIUM BY WEIGHING AS OXIDE

BeO taken (g)	*BeO found (g)*	*Error (g)*
0.0077	0.0076	−0.0001
0.0077	0.0077	0.0000
0.0154	0.0153	−0.0001
0.0154	0.0152	−0.0002

In another series of experiments beryllium was precipitated as described above, the precipitate was heated at 50–60° for 15 min with occasional stirring, filtered on No. 3 sintered glass crucible, washed with warm water (50–60°) and dried at 110° to constant weight. The metal content was calculated on the above theoretical percentage (2.08%) of beryllium. The results are given in Table II.

TABLE II

DETERMINATION OF BERYLLIUM BY WEIGHING THE PRECIPITATE DIRECTLY

Be taken (g)	*Weight of ppt. (g)*	*Be found (g)*	*Error (g)*
0.00277	0.1328	0.00277	0.00000
0.00277	0.1339	0.00278	+0.00001
0.00139	0.0666	0.00138	−0.00001
0.00139	0.0660	0.00137	−0.00002
0.00083	0.0406	0.00084	+0.00001
0.00055	0.0270	0.00056	+0.00001
0.00055	0.0272	0.00056	+0.00001

Effect of concentration of benzoylphenylhydroxylamine

The precipitation of beryllium was carried out using different amounts of the reagent, the other conditions remaining the same. It was observed that the precipitation of the metal was complete when the supernatant solution contained 0.1% (w/v) of the reagent in excess at pH 6.0.

Effect of pH

When the solutions of beryllium were adjusted to different pH values with dilute ammonia (3 *N*) after adding benzoylphenylhydroxylamine (two and half times the theoretical quantity), it was found that the precipitation of the metal commenced at pH 4.6 and was complete between pH 5.0 and 8.0. The pH values were measured with the aid of a Cambridge pH meter (bench model).

SEPARATION OF BERYLLIUM FROM IRON AND ALUMINIUM

A mixture containing known amounts of beryllium nitrate and aluminium nitrate or/and ferric nitrate was diluted to 300 ml, acidified with a few drops of dilute sulphuric acid and a 10% (w/v) solution of sodium acetate was added to adjust the pH to 4.0. The solution was heated to about 65° and benzoylphenylhydroxylamine (0.4–0.9 g dissolved in 10–15 ml of alcohol) was added to precipitate iron or/and aluminium. The precipitate was heated on a boiling water-bath for 1–1½ h with occasional stirring, filtered and washed with hot water containing 0.1% (w/v) reagent and sufficient acid to adjust the pH to 4.0.

The filtrate and washings were concentrated to 200 ml and filtered if any organic matter appeared owing to prolonged heating of the reagent solution in air. Benzoylphenylhydroxylamine (0.1–0.15 g dissolved in 5 ml of alcohol) was then added to the beryllium solution and the metal was precipitated and weighed as $Be(C_{13}H_{10}O_2N)_2$ as described above. The results given in Table III indicate that it is possible to separate beryllium quantitatively from iron or/and aluminium by the use of benzoylphenylhydroxylamine.

TABLE III

SEPARATION OF BERYLLIUM FROM IRON AND ALUMINIUM

Be taken (g)	*Foreign metal added (g)*		*Weight of ppt. (g)*	*Be found (g)*	*Error (g)*
	Fe(III)	*Al*			
0.00295	0.004	—	0.1425	0.00296	+0.00001
0.00295	0.008	—	0.1421	0.00295	0.00000
0.00295	0.019	—	0.1424	0.00296	+0.00001
0.00295	0.038	—	0.1410	0.00293	—0.00002
0.00295	0.038	—	0.1416	0.00294	—0.00001
0.00295	—	0.003	0.1423	0.00296	+0.00001
0.00295	—	0.007	0.1430	0.00297	+0.00002
0.00295	—	0.017	0.1416	0.00294	—0.00001
0.00295	—	0.034	0.1417	0.00294	—0.00001
0.00295	—	0.034	0.1412	0.00293	—0.00002
0.00295	0.004	0.003	0.1418	0.00294	—0.00001
0.00295	0.004	0.007	0.1426	0.00296	+0.00001
0.00295	0.008	0.007	0.1415	0.00293	—0.00002
0.00295	0.019	0.017	0.1415	0.00293	—0.00002

SEPARATION OF BERYLLIUM AND TITANIUM

Known volumes of beryllium nitrate and titanium sulphate solutions were taken, diluted to 300 ml, neutralised with 6 *N* ammonia and acidified with concentrated hydrochloric acid (3–4 ml). Titanium was precipitated by adding benzoylphenylhydroxylamine (0.4–0.7 g dissolved in 10 ml alcohol) with constant stirring. The titanium precipitate was allowed to stand for 45 min with occasional stirring, filtered and washed with dilute hydrochloric acid containing the organic reagent. The wash-liquid was prepared by adding 1 g of benzoylphenylhydroxylamine dissolved in 10 ml of alcohol to 1 l of warm distilled water, which was then cooled and mixed with 3 ml of concentrated hydrochloric acid. The filtrate and washings were concentrated, filtered and beryllium was determined as before. The results are shown in Table IV.

TABLE IV

SEPARATION OF BERYLLIUM FROM TITANIUM

Be taken (g)	*Ti added (g)*	*Weight of ppt. (g)*	*Be found (g)*	*Error (g)*
0.00295	0.002	0.1420	0.00295	0.00000
0.00295	0.003	0.1423	0.00296	+0.00001
0.00295	0.008	0.1418	0.00294	−0.00001
0.00295	0.017	0.1420	0.00295	0.00000
0.00295	0.017	0.1416	0.00294	−0.00001

Further work on the determination of beryllium in presence of other ions is in progress.

ACKNOWLEDGEMENT

The sample of benzoylphenylhydroxylamine was kindly supplied by E. Merck, Darmstadt, Germany.

SUMMARY

N-Benzoylphenylhydroxylamine has been employed in the gravimetric determination of beryllium and in its separation from iron, aluminium and titanium. After suitable adjustment of pH iron, aluminium or titanium is precipitated quantitatively with the reagent; beryllium is subsequently precipitated after raising the pH of the filtrate. The metal may be determined by either igniting the precipitate to beryllium oxide or weighing it as $Be(C_{13}H_{10}O_2N)_2$.

RÉSUMÉ

La N-benzoylphénylhydroxylamine est proposée comme réactif pour le dosage gravimétrique du béryllium. Une séparation du béryllium est alors possible d'avec le fer, l'aluminium et le titane.

ZUSAMMENFASSUNG

Zur gravimetrischen Bestimmung von Beryllium und seine Trennung von Eisen, Aluminium und Titan kann N-Benzoylphenylhydroxylamin verwendet werden.

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IMPURITY DETERMINATION BY THERMAL ANALYSIS

II. THE MELTING CURVE OF A QUICKLY FROZEN SAMPLE

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INTRODUCTION

The heating curve of a gradually frozen sample was discussed in a previous paper[1]. The melting curve of a sample obtained by quick freezing is now considered.

When a liquid sample is cooled rapidly to far below its freezing point, *total* equilibrium is excluded. It is hardly even likely that local equilibrium (in the sense of part I) is present. Sudden freezing of a sample often results in a homogeneous solid solution*. Intermediate stages between a build-up of the solid according to the local equilibrium theory (part I) and a homogeneous solid solution may occur, depending on the rate of cooling. These intermediate stages are likely to be badly reproducible and are not suitable for mathematical treatment. Therefore the present discussion is restricted to the melting curve of a homogeneous solid solution.

The melting curve of a homogeneous solid solution

The diffusion of the solid is assumed to be virtually restricted to a surface layer at the interface of solid and liquid. The liquid is assumed to be homogeneous. Little is known about the amount of substance contained in the surface layer. It can only be stated that it usually is maximal when melting starts and approaches zero when melting becomes complete. The concentration within the surface layer is a function of the distance from the interface. The surface layer is assumed to act in the same way as a solid fraction (f) of the sample which is in equilibrium with the liquid. The problem will be treated as if such a fraction f, having a concentration X_S is really present. Obviously f is a function of y.

Suppose a fraction y of the sample has melted. Since the surface layer is assumed to be in equilibrium with the liquid, the total fraction of the sample participating in the equilibrium may be represented by $(y + f)$. According to the law of conservation of matter:

$$(y + f)X = yX_L + fX_S \qquad (1)$$

where X is the concentration of the total sample and X_L the concentration in the liquid. When X_S and X_L are small, $X_S/X_L = k$ (constant) is valid. Thus

* Indications have been obtained that systems normally forming no solid solutions may form a supersaturated solid solution on quick freezing.

$$\left(\frac{y+f}{Y+kf}\right) X = X_L \tag{2}$$

Moreover when X_L is small: $X_L = k_L \Delta T$ is approximately valid. Consequently the following relation between ΔT and y may be considered as a fair approximation:

$$\Delta T = \frac{X}{k_L}\left(\frac{y+f}{y+kf}\right) \tag{3a}$$

or since X/k_L equals the depression of the final melting point (ΔT_m) of the sample:

$$\Delta T = \Delta T_m \left(\frac{y+f}{y+kf}\right) \tag{3b}$$

Discussion of the equations (3a) and (3b)

When no miscibility occurs in the solid, the whole solid has permanently the same concentration and may be considered to be in equilibrium with the liquid. Then f equals $(1-y)$. Since in that case $k = 0$, eqn. (3a) reduces to the well known White equation.

In order to avoid possible misunderstandings it should be noted that the following discussion is restricted to solid solutions. It has already been mentioned, that f is a function of y, being zero at $y = 1$. Little more is known about f. It can only be stated that f also depends on the shape and size of the crystals. When tiny crystals are formed the area of the interface of solid and liquid and thus f, may be large. The ultimate value of f equals $(1 - y)$. Then eqn. (3a) becomes eqn. (9) of part I, which is valid for total equilibrium[1].

Especially when tiny or imperfect crystals are present f is also a function of time. For, as may be known, perfect and large crystals have a tendency to grow at the cost of small or imperfect crystals. When f is relatively small the temperature of the sample approaches its final melting point soon after melting has started (see eqn. 3b). Thus superheating of the bulk of the solid must occur, unless an additional interface is formed. Since the formation of new interface occurs by passing an energy barrier, the temperature of the sample may decrease suddenly when the new interface is formed. The formation of the new interface in the solid may be compared with the formation of a vapour bubble in a liquid. As is the case with superheating of liquids, the extent of superheating of solid solutions is unpredictable.

So f may change discontinuously to an unknown extent. It is thus clear that a quantitative experimental proof of eqns. (3a) and (3b) is impossible.

However, the foregoing permits a number of qualitative conclusions which can be checked by experiment:

The melting curve of a sample of solid solutions obtained by quick freezing may show the following features, *viz.*

(*1*) The temperatures observed will be higher than the corresponding temperatures of a curve calculated on the basis of total equilibrium (see ref.[1], eqn. 9) or at least be equal to these.

(*2*) The difference between the temperatures observed and those obtaining to a "total equilibrium curve" will be larger when the sample has been stored for a long time (preferably at elevated temperatures).

(3) After prolonged storage of the sample, its melting curve may resemble the curve of an extremely pure substance.

(4) Depending on the rate of formation of new interfaces, the melting curve of such a sample may show a maximum.

TABLE I

DEPRESSIONS FOUND AND CALCULATED ON A QUICKLY FROZEN SAMPLE OF DIPHENYL CONTAINING 0.181 mol% PHENANTHRENE

Fraction liquid	*ΔT found*			*ΔT calculated according the total equilibrium theory*
	without annealing	*after 3 h annealing*	*after 10 days annealing*	
0.1	0.13	0.11	0.10	0.22
0.2	0.09	0.08	0.08	0.18
0.3	0.08	0.08	0.08	0.14
0.4	0.08	0.08	0.08	0.12
0.5	0.08	0.08	0.08	0.10
0.6	0.08	0.08	0.08	0.09
0.7	0.08	0.08	0.08	0.08
1.0	0.07	0.08	0.08	0.07

TABLE II

DEPRESSIONS FOUND AND CALCULATED ON A QUICKLY FROZEN SAMPLE OF DIPHENYL CONTAINING 0.762 mol% OF PHENANTHRENE

Fraction liquid	*ΔT found*			*ΔT calculated according the total equilibrium theory*
	without annealing	*after 3 h annealing*	*after 10 days annealing*	
0.1	0.79	0.67	0.40	0.95
0.2	0.65	0.59	0.38	0.77
0.3	0.59	0.55	0.37	0.64
0.4	0.55	0.52	0.37	0.55
0.5	0.51	0.49	0.37	0.49
0.6	0.43	0.46	0.37	0.43
0.7	0.40	0.40	0.36	0.39
1.0	0.30	0.30	0.30	0.30

TABLE III

DEPRESSIONS FOUND AND CALCULATED ON A QUICKLY FROZEN SAMPLE OF TIN CONTAINING 0.300 mol% OF BISMUTH

Fraction liquid	*ΔT found*			*ΔT calculated according the total equilibrium theory*
	without annealing	*after 3 h annealing*	*after 10 days annealing*	
0.1	1.80	1.51	1.10	1.84
0.2	1.39	1.34	0.98	1.40
0.3	1.20	1.20	0.88	1.22
0.4	1.07	1.05	0.80	1.08
0.5	0.97	0.95	0.75	0.98
0.6	0.90	0.87	0.69	0.90
1.0	0.65	0.65	0.65	0.64

EXPERIMENTS

The samples used in the quick freezing experiments were the same samples as used during the experiments on gradual freezing (see part I). The heating curves were determined with the thin-film apparatus[2,3]. The samples were melted in the measuring vessel and then frozen within 10–25 sec. After the sample had been stored for a definite time, its melting curve was determined. The experimental results, which are summarised in Tables I, II and III, illustrate the first three conclusions; see p. 42). Fig. 1 may be considered as an illustration of conclusion 4. The curve presented was obtained with a sample of tin containing 0.300 mol % of bismuth. The sample was quickly frozen and then stored for three hours at a temperature of 228°. Analogous curves were obtained on previous occasions with organic substances[4].

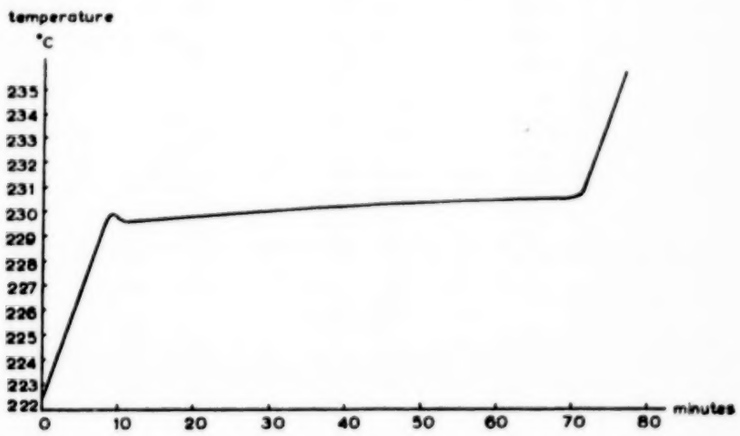

Fig. 1. Melting curve of a quickly frozen solution of 0.300 mol % bismuth in tin after three hours of annealing at 228°.

DISCUSSION

This discussion is restricted to solid solutions obtained by quick freezing.

Since so little is known about the function f, which is determined by the behaviour of the diffusion layer, it must be concluded that an impurity determination based on only one curve of a quickly frozen sample is of dubious value. As already mentioned it may happen that f equals $(1-y)$. This may occur when a complex of conditions is fulfilled, *viz.*

(*a*) the rate of diffusion in the solid is relatively high; the sample consists of a large number of tiny and imperfect crystals with only a small tendency to transform into large and perfect crystals;

(*b*) the melting curve is determined according to a quasi static method, the sample being kept under adiabatic conditions only to the extent required to obtain a constant temperature after addition of a certain amount of heat.

These conditions seem to have been met previously[5] during the determination of the melting curve of a sample of diphenyl contaminated by phenanthrene. At least it appeared that the equation for total equilibrium was applicable in that case. However, in several other cases the conditions for attainment of total equilibrium seem to be absent. BADLEY[6], for instance, investigated a number of quickly frozen samples of solid solutions and found his impurity determinations invariably low. In some cases only 6% of the amount of impurity added could be traced.

It may be useful to note here that the comparative method is applicable to quickly frozen samples, provided that the function f of the two samples to be compared is the same. Then, as can be shown easily, eqn. (12) of part I is valid[1].

Since it appears that the same equation of the comparative method is applicable to samples showing total equilibrium as well as to both gradually or quickly frozen samples, it is comprehensible that the comparative method yields acceptable results in so many cases.

The comparative method only demands the same pretreatment of both samples to be compared. Any special treatment is not required. Nevertheless it should be stressed that quick freezing is not recommended, even when the comparative method is applied. In addition to the risk of unforeseen variations in the behaviour of the quickly frozen sample, it should be remembered that quickly frozen mixtures show smaller depressions than any other mixture does.

ACKNOWLEDGEMENT

We wish to thank Mr. A. VAN KUYK for his accurate measurements.

SUMMARY

A temperature-heat content relation is derived for a homogeneous solid solution of a binary system showing a very restricted rate of diffusion in the solid. It is shown experimentally that quickly frozen samples behave like homogeneous solid solutions. According to the new theory the depressions determined on partly molten samples are usually small and depend on the conditions; thus purity determinations based on heating curves of quickly frozen samples are of dubious value. The theory shows that superheating of the solid may occur when a solid solution is melted; this is confirmed experimentally.

RÉSUMÉ

Lors de leur étude sur la détermination des impuretés par analyse thermique, les auteurs ont constaté que des échantillons refroidis rapidement se comportaient comme des solutions homogènes solides.

ZUSAMMENFASSUNG

Bei Bestimmungen des Reinheitsgrades durch thermische Analyse wurde gefunden, dass sich rasch abgekühlte Proben wie homogene feste Lösungen verhalten.

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THE ASSAY OF SODIUM CITRATE AND SODIUM POTASSIUM TARTRATE BY CATION EXCHANGE AND NON-AQUEOUS TITRIMETRY

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INTRODUCTION

The official methods of the British Pharmacopoeia and of the B.P.C. for the assays of salts of organic acids, are time consuming and the burning and the transference stages require considerable care in order to avoid errors.

The B.P. assay gives a somewhat indirect measure of cation present by titrating the carbonate formed on carbonising the organic salt, whereas the cation exchange technique gives a direct measure of the anion, and non-aqueous titrimetry a direct measure of the cation.

(A) ASSAY BY CATION EXCHANGE RESINS

Investigation into suitability of conditions

Choice of indicator

For the titration of the liberated acids: Thymol blue was found to be the best indicator for citric acid and phenolphthalein for tartaric acid.

Column time

Experiments to determine the minimum time necessary for sodium citrate solution to pass through the column and also for minimum time for washing were carried out. As a result of these experiments a 20-min column time and a 20-min column wash time were found to be necessary, using the quantities of distilled water stated in *Method* below.

Column loading

In order to avoid the possibility of overloading the resin column it was concluded that not more than two assays should be carried out on the same resin column.

Method

Sodium citrate and sodium potassium tartrate assay by cation exchange resin, Amberlite I.R.120(H)

Principle. An ion exchange method employing Amberlite resin I.R.120(H), the effluent from the column containing the free acid is titrated with standard sodium hydroxide.

Apparatus. An all glass column 1.8 cm in diameter, with a 7.5-cm layer of resin supported on a sintered glass disc (porosity 1). When a fresh column is prepared it should be backwashed with distilled water to displace trapped air and also to wash away fine particles of dirt and resin.

Regeneration of (used and fresh) resin. Pass 300 ml of hydrochloric acid (4 *N*) through the column, this should take about 90 min. Follow this with a distilled water wash of about 2½ l, continue washing until the effluent no longer gives an acid reaction to methyl orange.

Reagents. Amberlite ion exchange resin I.R.120(H). Phenolphthalein indicator solution, 0.2% w/v in 60% v/v industrial methylated spirits. Methyl orange indicator solution, 0.04% w/v in 20% v/v industrial methylated spirits. Thymol blue indicator solution, dissolve 0.1 g thymol blue in 4.3 ml *N*/20 sodium hydroxide solution and 5 ml industrial methylated spirits with a little heat, dilute to 250 ml with 20% v/v industrial methylated spirits. 0.1 *N* sodium hydroxide, accurately standardised against potassium hydrogen phthalate. Hydrochloric acid, 4 *N*.

Procedure. Grind 5–6 g sample in a clean dry mortar to a fine powder. Accurately weigh 0.4 g in the case of sodium citrate and 0.6 g in the case of sodium potassium tartrate and quantitatively transfer to a 100-ml beaker, add 30 ml distilled water, warm to aid solution and when dissolved, transfer to a tap-funnel above the ion exchange column and dilute to about 75–80 ml. Allow the solution to run through the column. This should take about 20 min. The head of solution above the resin should be maintained at between 1.5 cm and 4.5 cm. Collect the effluent in a 400-ml conical beaker. Wash down the inside of the tap funnel and run a further 100 ml of distilled water through the column taking about 20 min and collecting the effluent in the same beaker. Wash the column through with a further quantity of 100 ml distilled water taking about 20 min for the water to go through the column and collect the effluent in another 400-ml beaker.

Evaporate the contents of both beakers down to about 15–20 ml, and allow to cool. Titrate with accurately standardised 0.1 *N* sodium hydroxide from a calibrated burette. In the case of sodium citrate use 5 drops of thymol blue indicator solution, and in the case of sodium potassium tartrate use 4 drops of phenolphthalein indicator solution.

The second beaker in each case should not require more than 0.1 ml 0.1 *N* sodium hydroxide. If the titration exceeds this amount, the assay should be repeated using freshly regenerated resin, as a larger titration in the second beaker is indicative of aged or poorly regenerated resin.

Calculation

If weight of sample = *S* g, and total titration = *A* ml, then

$$\text{assay} = \frac{A}{S} \cdot 0.009804 \cdot 100\% \text{ sodium citrate } (Na_3C_6H_5O_7 \cdot 2H_2O)$$

$$= \frac{A}{S} \cdot 0.01411 \cdot 100\% \text{ sodium potassium tartrate } (NaKC_4H_6O_6 \cdot 4H_2O)$$

Notes

1. The resin must be washed free from acid immediately prior to use.

2. On no account must resin as received be used — it must be regenerated first.
3. The resin must be regenerated after two determinations or freshly regenerated resin used.
4. The resin can be more conveniently regenerated in bulk.

(B) ASSAY BY NON-AQUEOUS TITRIMETRY

(a) Sodium citrate assay, by titration with 0.1 N acetous perchloric acid

Investigation into the suitability of conditions

Choice of indicator

The equivalent point — a purple coloration — with Oracet Blue B is much more easily detected than the equivalent point — a green coloration — with Crystal Violet. Quinaldine Red was also tried but no easily detectable end-point was observed.

Although the use of visual indicators (particularly Oracet Blue B) is fairly satisfactory, it has been found that the most reliable and accurate end-point detection is the potentiometric procedure as described under *(b)*. The potentiometric method was used for the majority of this work.

Choice of primary standard

Potassium hydrogen phthalate was found to be most suitable because of the usual factors: high equivalent weight, high purity, non-hygroscopic salt, etc. The precipitate of potassium perchlorate formed during the titration can be safely ignored and has no adverse effect on the accuracy, particularly if the potentiometric method is used

Choice of grade of acetic acid

The special grade of acetic acid "low water content acetic acid for non-aqueous titrations" is by far the best, but if the potentiometric method is used, "Laboratory Grade" has been found to be quite suitable. If "Laboratory grade" acetic acid is used, however, it is preferable to determine the water content by the Karl Fischer method and adjust the water content to 0.01 to 0.1% by means of acetic anhydride if necessary.

Effect of the presence of water

In the case of titration using Oracet Blue B as indicator, the end-point was found to be affected by the presence of water; increasing amounts of water giving increasing titrations and progressively more indistinct end-points. Addition of water at the end-point of the titration of 50 ml of the sodium citrate solution in glacial acetic acid gave the following results (Table I).

TABLE I

ml water added	*Additional titration required to the titration of 50 ml acetous sodium citrate solution (50 ml = 0.4 g) in order to reach the end-point on addition of the amounts of water shown (ml)*
0.2	0.15
0.5	0.40
1.0	0.90
2.0	1.81[a]

[a] end-point very indistinct

Method

Principle. Sodium citrate is dissolved in glacial acetic acid and its enhanced basicity titrated with acetous perchloric acid, detecting the end-point potentiometrically.

Apparatus. Magnetic stirrer. Direct reading pH meter, Pye model, Cat.No.11067. pH meter EMF "backing off" accessory, see *(b)*. Glacial acetic acid reference electrode, E.I.L. Type RJ/24/5. Glass electrode, Pye Cat. No.11126.

Reagents. Glacial acetic acid. 0.1 *N* acetous perchloric acid, see Notes.

Procedure. Grind 5–6 g of sample to a fine powder and transfer 0.4 g, accurately weighed, to a 150-ml beaker, add 75 ml glacial acetic acid, warm to aid solution and allow to cool, under moisture-free conditions. Place the beaker on the magnetic stirrer, place the electrodes in position, switch the pH meter EMF 'Backing off' accessory on and switch the pH meter to 0–800-mV range. Adjust the meter reading to 700 mV using the variable resistance on the pH meter EMF' backing off' accessory and the set zero as fine control. Set the stirrer in motion and titrate with 0.1 *N* acetous perchloric acid until the meter registers 480 mV (*i.e.* the end-point) and read the burette.

Calculation

If weight of sample taken = S g, and corrected burette reading = V ml, then

$$\text{assay} = \frac{V}{S} \cdot 0.009804 \cdot 100\% \text{ sodium citrate } (Na_3C_6H_5O_7 \cdot 2H_2O)$$

See also Appendix for temperature corrections.

Notes

The end-point is the point of inflexion in the curve obtained by plotting mV against ml titrant. A more accurate method of finding the end-point is to plot the first derivative against ml titrant; the maxima of the curve thus gives the end-point (See Figs. 2 and 3).

Preparation and standardisation of 0.1 N acetous perchloric acid

Transfer 1800 ml glacial acetic acid to a 2-l beaker, add very slowly with continuous stirring with the magnetic stirrer, 17.0 ml of perchloric acid (72%), followed by 60 ml of acetic anhydride. Transfer to a 2-l volumetric flask and dilute to 2 l with glacial acetic acid and allow to stand for 24 h. Standardise against 1.0 g (accurately weighed) potassium hydrogen phthalate using the above procedure.

(b) Sodium potassium tartrate assay by addition of an excess of 0.1 N acetous perchloric acid and back titration with 0.1 N acetous potassium acetate

Introduction

Sodium potassium tartrate is only slightly soluble in glacial acetic acid, due to the formation of potassium hydrogen tartrate. Hence a direct titration with acetous perchloric acid is very slow, taking about 15–20 min, but this has been found to give the correct result.

The assay, however, can be carried out by the following procedure, but the end-point is far from distinct using either Oracet Blue B or crystal violet indicators:

Transfer 0.6 g sample to a 150-ml B 24 neck flat-bottomed flask, add 50 ml 0.1 *N* acetous perchloric acid accurately, and stir the stoppered flask for at least 20 min. Then back titrate this solution with 0.1 *N* acetous sodium acetate or 0.1 *N* acetous potassium acetate.

Potentiometric procedure

A suitable electrode system consists of a glass electrode as indicator electrode with a saturated calomel half-cell of the 'sleeve' type as reference electrode. Care must be taken to prevent leakage of potassium chloride from the calomel electrode into the titration liquid, as this leads to vitiation of results due to the interaction of the potassium chloride with the perchloric acid titrant. (In view of this difficulty a specially constructed glacial acetic acid/mercurous acetate reference electrode was subsequently used).

The glass and reference electrodes are connected to a direct reading pH meter and the titration curve drawn by plotting the readings of either the mV- (or the pH scale) as ordinates, and the corresponding volumes as abscissae.

When a glass/calomel electrode system is immersed in an aqueous solution, the glass electrode usually assumes a negative potential with respect to the calomel electrode, but in glacial acetic acid, the glass electrode may assume a positive potential with respect to the calomel electrode, a phenomenon which may also occur in aqueous solution of low pH.

It is, therefore necessary to connect an auxilliary source of EMF in series with the electrodes in such a fashion as to "back off" a proportion of the electrode EMF. For routine titrations a 1.5-V dry cell in conjunction with a potential divider, is suitable, a convenient arrangement is shown in the diagram (Fig. 1).

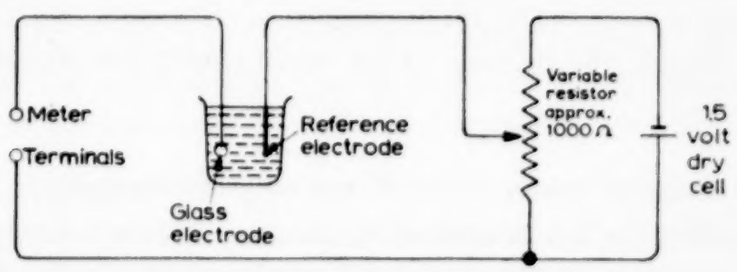

Fig. 1. EMF backing off accessory.

It is advisable to place the electrode system under a fume hood, as the vigorous stirring necessary to mix the solutions during a titration results in the dissipation of much acetic acid vapour. This is unpleasant for the operator and may cause corrosion and damage to the instrument.

The results may be represented either as a direct titration curve (Fig. 2) in which uncorrected meter readings are plotted as ordinates and the corresponding titration readings as abscissae, or as a differential curve $(\Delta mE)/\Delta V$ as ordinate and the corresponding titration reading as abscissae; where ΔmE is a small change in mV, and ΔV the corresponding change in volume of titrant (Fig. 3).

Time of stirring

The time for which the sodium potassium tartrate and 50 ml 0.1 *N* acetous per-

chloric acid is stirred is critical. A minimum period of 20 min was found to be necessary.

Choice of back titrant

From the titration curves of 0.1 *N* acetous sodium acetate titrated against standard 0.1 *N* acetous perchloric acid and 0.1 *N* acetous potassium acetate titrated against standard 0.1 *N* acetous perchloric acid it was found that acetous potassium acetate had the higher maxima on plotting the first derivative $(\Delta mE)/\Delta V$ against V. Hence acetous potassium acetate is preferred (see Figs. 2 and 3).

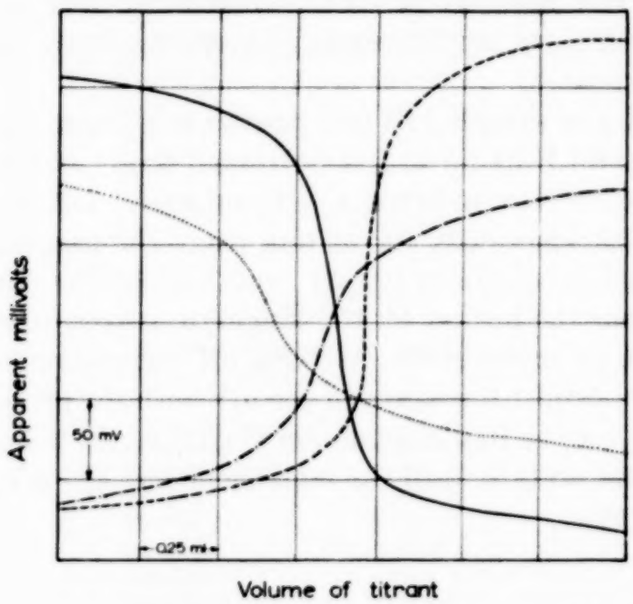

Fig. 2. Titration curves ———— Standardisation of acetous perchloric acid against potassium hydrogen phthalate; — — — Standardisation of acetous potassium acetate against acetous perchloric acid; . . . . . Sodium citrate assay; · — · — · Sodium potassium tartrate assay.

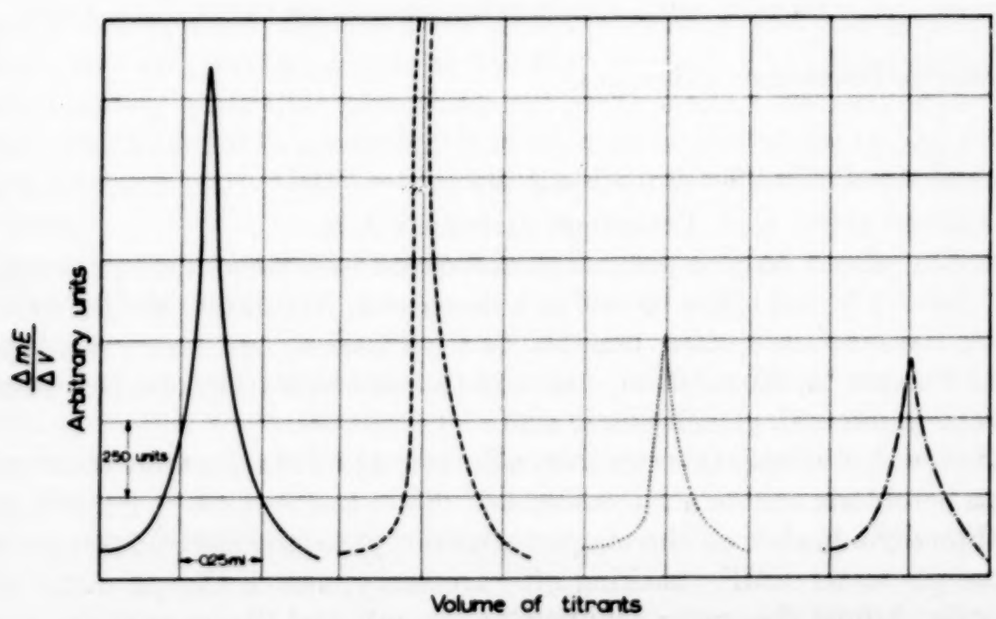

Fig. 3. First derivative curves. ———— Standardisation of acetous perchloric acid against potassium hydrogen phthalate; — — — Standardisation of acetous potassium acetate against acetous perchloric acid; . . . . . Sodium citrate assay; · — · — · Sodium potassium tartrate assay.

Method

Principle. The sodium potassium tartrate is stirred with excess standard acetous perchloric acid which reacts with the enhanced basicity of the salt. The excess of acetous perchloric acid is then back titrated with standard acetous potassium acetate, the end-point being determined potentiometrically. The precipitate of potassium perchlorate has no adverse effect on the titration.

Apparatus. Magnetic stirrer. Direct reading pH meter, Pye Model, Cat. No. 11067. pH meter EMF "backing off" accessory, as described above. Glacial acetic acid reference electrode, E.I.L. Type RJ24/5. Glass electrode, Pye Cat. No. 11126.

Reagents. Glacial acetic acid. 0.1 *N* acetous perchloric acid, standardised against potassium hydrogen phthalate. 0.1 *N* acetous potassium acetate, standardised against 0.1 *N* acetous perchloric acid.

Procedure. Grind 5–6 g of sample to a fine powder in a mortar, transfer 0.6 g accurately weighed to a 150-ml B.24 neck, flat bottomed flask, add 50 ml 0.1 *N* acetous perchloric acid from a burette, insert a 2.5-cm magnetic follower, stopper and stir the contents of the flask vigorously for 20 min using the magnetic stirrer. Transfer the contents of the flask to a 150-ml beaker, washing out the flask with a stream of glacial acetic acid. Place the beaker on the magnetic stirrer, place the electrodes in position, switch on the pH meter EMF "backing off" accessory, switch the pH meter to the 0–800-mV range. Adjust the meter to 300 mV with the pH meter EMF "backing off" accessory and set zero as fine control. Set the stirrer in motion and titrate with 0.1 *N* acetous potassium acetate until the meter registers 470 mV (*i.e.* the end-point) and then read the burette.

Calculation

If weight of sample taken = S g, if corrected volume of 0.1 *N* acetous perchloric acid = V_1 ml, and corrected volume of 0.1 *N* acetous potassium acetate = V_2 ml, then

$$\text{assay} = \frac{(V_1 - V_2)}{S} \cdot 0.01411 \cdot 100\% \text{ sodium potassium tartrate } (NaKC_4H_6O_6 \cdot 4H_2O)$$

See the Appendix for temperature corrections.

Preparation and standardisation of acetous potassium acetate

Reagents. Glacial acetic acid. Potassium carbonate A.R.

Procedure. Dry about 20 g of potassium carbonate in a nickel dish in an electric oven at 150° for 2–3 h, and allow to cool in a desiccator. Accurately weigh out 6.91 g of the dried potassium carbonate, transfer to a 1-l beaker, add 200–300 ml glacial acetic acid and warm to aid solution, cool and transfer to a 1-l graduated flask and make up to the mark with glacial acetic acid.

Standardisation. Accurately transfer from a burette 45 ml of accurately standardised 0.1 *N* acetous perchloric acid to a 150-ml beaker, dilute to about 70–75 ml with glacial acetic acid. Place the beaker on the magnetic stirrer, place the electrodes in position, switch on the pH meter EMF "backing off" accessory, switch the pH meter to the 0–800 mV scale. Adjust the meter readings to 300 mV and titrate with the acetous potassium acetate until a meter reading of 480 is obtained, *i.e.* the end-point, and read the burette.

Calculation

Normality of acetous potassium acetate in terms of the normality of the 0.1 N acetous perchloric acid = A/B normal.

Where A = volume of 0.1 N acetous potassium acetate taken

B = volume of 0.1 N acetous potassium acetate required, and hence temperature or burette corrections are not required.

RESULTS

TABLE II

SODIUM CITRATE

Sample	*Assay by*		
	B.P. method	*Ion exchange*	*Non-aqueous*
1	99.8%	99.6%	99.7%
2	99.2%	99.3%	99.1%
3	99.7%	99.8%	99.7%
4	99.4%	99.5%	99.5%
5	99.5%	99.7%	99.7%
6	99.8%	99.8%	99.7%

TABLE III

SODIUM POTASSIUM TARTRATE

Sample	*Assay by*		
	B.P. method	*Ion exchange*	*Non-aqueous*
1	99.6%	99.5%	99.6%
2	99.9%	100.1%	100.0%
3	99.5%	99.6%	99.3%
4	100.0%	100.1%	100.0%
5	99.8%	99.7%	100.0%
6	99.3%	99.5%	99.4%

CONCLUSIONS

Hence it can be seen that both the cation exchange and non-aqueous titrimetry methods give very similar results to the B.P. method. The cation exchange method is unfortunately quite time consuming but gives a direct measure of the organic acid present, which cannot be conveniently or accurately carried out by any other method. It is, however, a convenient method for the determination of total anion content of acid salts.

The non-aqueous method, however, is much more rapid and less time consuming than the B.P. method.

Hence, in conclusion, the method of titration with perchloric acid in anhydrous acetic acid offers considerable advantages over the official methods used for the assays of salts of organic acids, because of its speed, simplicity and standardisation of procedure without any loss of accuracy. The major criticism of the method is the effect of the high coefficient of expansion of acetic acid solutions compared with aqueous solutions; but, however, a corrective factor can readily be applied — see Appendix.

APPENDIX

Temperature corrections

Multiply the volume of titrant by $1 - (t \cdot 0.001)$, if the titration is carried out at a

temperature above 20° or by $1 + (t \cdot 0.001)$, if the temperature is below 20°. (t = difference in ° from 20°).

ACKNOWLEDGEMENTS

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SUMMARY

Sodium citrate and sodium potassium tartrate are assayed by passing aqueous solutions of the salts through cation exchange resin columns, concentrating the effluents from the columns, and then titrating the effluents with standard sodium hydroxide solution. Sodium citrate is assayed by titrating a solution of the salt in glacial acetic acid with standard acetous perchloric acid, the end-point being detected potentiometrically; sodium potassium tartrate is assayed by stirring the salt in excess standard acetous perchloric acid, and then backtitrating the excess acetous perchloric acid with standard acetous potassium acetate, the end-point being detected potentiometrically.

RÉSUMÉ

Une méthode est proposée pour le dosage du citrate de sodium et du tartrate sodicopotassique par passage sur une résine, échangeur de cations, et titrage potentiométrique en milieu non-aqueux. Le citrate de sodium est titré, en solution dans l'acide acétique glacial, par une solution acétique d'acide perchlorique; le tartrate est traité par la solution acétique d'acide perchlorique et titré en retour par une solution étalon d'acétate de potassium.

ZUSAMMENFASSUNG

Natriumcitrat und Kalium-natriumtartrat können nach Behandlung mit einem Kationen-Austauscherharz im Eluat durch Titration mit Natriumhydroxydlösung bestimmt werden. Natriumcitrat, in Eisessig gelöst, kann mit Eisessig-Perchlorsäure titriert werden unter potentiometrischer Bestimmung des Endpunktes. Kalium-natriumtartrat wird mit einem Ueberschuss von Eisessig-Perchlorsäure versetzt und der Ueberschuss mit Kaliumacetat-Eisessiglösung zurücktitriert, wobei der Endpunkt ebenfalls potentiometrisch bestimmt wird.

MICRODOSAGE DU COBALT DANS LE „ZIRCONIUM REACTOR-GRADE"

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Parmi les matériaux entrant dans la constitution des réacteurs atomiques, le zirconium et ses alliages occupent une place importante du fait de leur grande résistance à la corrosion par l'eau et les métaux fondus, de leur faible section efficace de capture des neutrons thermiques, de leur bonne conductibilité de la chaleur et de leur stabilité mécanique (absence de déformation sous l'influence du rayonnement). Ils conviennent particulièrement bien pour enrober les barreaux d'uranium.

Le contrôle de la pureté du métal et de ses alliages est un problème important car les tolérances admises, variables suivant la nature de l'impureté, sont souvent très faibles, notamment en ce qui concerne le cobalt.

Quelques méthodes de dosage du cobalt dans le zirconium ont été proposées dernièrement. Dans l'une[1], les auteurs déterminent le cobalt par spectrophotométrie de son complexe avec le nitroso-1-naphtol-2, après extraction de celui-ci par le chloroforme. On a fait également appel à une séparation électrolytique sur cathode de mercure[2]; après distillation de ce dernier, on dose le cobalt dans le résidu par spectrophotométrie en présence de nitroso-sel R. La prise est de 1 g dans chaque cas. La première méthode donne de bons résultats avec des quantités de cobalt comprises entre 0.5 et 30 μg par ml de solution finale. La seconde, plus sensible, va de 5 à 0.1 μg/ml. La détermination du cobalt à l'aide de nitroso-sel R a également été faite sans séparation préalable[3], mais la présence de certains ions peut alors perturber le dosage.

Après l'étude que nous avons faite concernant la séparation et le dosage de traces de cobalt dans différents milieux minéraux et organiques[4], nous avons constaté qu'il est avantageux de mettre à profit la grande sensibilité de la méthode spectrophotométrique utilisant le nitroso-sel R et la qualité des séparations obtenues en utilisant la résine Dowex 1-X8, pour effectuer des dosages sur des prises aussi faibles que possibles. On réduit ainsi la durée de la plupart des opérations telles que mise en solution, extraction, évaporation, etc. C'est pourquoi nous proposons une méthode permettant de doser le cobalt sur des prises de 100 mg de zirconium très pur (type RG.SG.101).

Principe de la méthode

Après solubilisation au moyen des acides nitrique, chlorhydrique et fluorhydrique, la solution obtenue est introduite dans une colonne échangeur d'ions contenant de la résine Dowex 1-X8. Le cobalt est séparé dans les conditions où l'on travaille. On purifie ensuite le cobalt élué par extraction à l'aide de dithizone, puis on minéralise

le dithizonate de cobalt et forme le complexe en présence de nitroso-sel R. On mesure la densité optique à 520 mμ par rapport à un blanc préparé dans les mêmes conditions. Lorsqu'on travaille sur des solutions contenant de très faibles quantités de cobalt, l'influence des pertes survenant au cours de l'analyse devient très importante, aussi avons nous utilisé du ^{60}Co comme traceur radioactif. Des mesures d'activité faites dans les mêmes conditions, au début et à la fin du dosage permettent de déterminer avec précision la valeur de ces pertes et de corriger les résultats en conséquence.

Les résultats proprement dits sont contrôlés d'autre part à l'aide de différents essais parallèles:

(a) Mesure spectrophotométrique (effectuée dans les mêmes conditions que l'analyse) d'une solution de cobalt pur dont la concentration, exactement connue, est voisine de celle de l'échantillon (étalon externe).

(b) Adjonction d'une quantité connue de cobalt dans la solution de l'échantillon (étalon interne). Après mesure et calcul du résultat d'après (a), on déduit la quantité de cobalt ajoutée. La valeur ainsi obtenue doit être égale à celle que donne un dosage fait sans adjonction de cobalt. De cette manière, on contrôle simultanément l'étalonnage (a) et l'absence d'effet gênant provenant de la solution (c).

(c) Adjonction d'une quantité connue de cobalt dans une fraction d'éluat recueillie immédiatement après le passage du cobalt de l'échantillon. L'étalon se trouve ainsi placé dans des conditions aussi voisines que possible de celles de l'analyse.

(d) Essais à blanc effectués dans les mêmes conditions que l'analyse.

Ces essais nous montrent une très bonne concordance entre les densités optiques obtenues dans ces différentes conditions. En pratique, les essais (a) et (b) sont à refaire avant chaque série d'analyses; l'essai (d) est à refaire lorsqu'on utilise de nouveaux réactifs.

Appareillage

Spectrophotomètre Beckman, modèle DU, avec photomultiplicateur permettant l'extention de la zone de lecture 90–100% sur toute la longueur de l'échelle.

Echelle décadique „Tracerlab", type SC-33A „1000 Scaler", avec sonde à scintillation P-20B équipée d'un cristal NaI(Tl) à puits.

Réactifs et solutions (Produits Merck pro anal.)

Acide chlorhydrique concentré et solutions 9 *N*, 4 *N*, 0.1 *N* et 0.01 *N*; acide nitrique concentré; acide perchlorique concentré; acide fluorhydrique 1/5; solution d'hydroxyde de sodium, concentrée (20 à 30%) et 1 *N*; solution de chlorure de sodium (ou KCl) 0.1 *M*; chlorure d'aluminium; citrate de sodium; éther; solution à 0.05% de dithizone dans l'éther; tampon acétique de pH 6 (solution d'acétate de sodium à 10% amenée au pH 6 par de l'acide acétique glacial); solution de nitroso-sel R à 0.05% dans l'eau (provenance Fluka); resine Dowex 1-X8 à anions $-N^+(CH_3)_3$ fortement basiques, de 100–200 mesh (provenance Fluka); solution de ^{60}Co ayant une activité de 0.025 μC/ml et une concentration de 0.0035 μg/ml. Cette solution sert de traceur radioactif (provenance Harwell).

Mise en solution

Le zirconium est insoluble dans les acides, même à chaud. La littérature propose pour le dissoudre, soit l'eau régale, soit l'acide fluorhydrique. L'attaque du zirconium

par l'eau régale est trop lente pour que ce réactif puisse être retenu; l'acide fluorhydrique, par contre, dissout très rapidement ce métal, même à froid (la réaction est vive), mais l'emploi de cet acide présente de multiples inconvénients (attaque des récipients, vapeurs corrosives, élimination difficile, etc.). C'est pourquoi nous avons appliqué un autre processus de mise en solution. Il se trouve que l'acide fluorhydrique est non seulement un excellent oxydant du zirconium mais également un catalyseur d'oxydation et l'expérience montre que de petites quantités d'acide fluorhydrique, introduites dans l'eau régale, suffisent pour accélérer considérablement l'attaque, même à froid.

L'attaque à chaud se fait déjà lorsque le rapport HF/eau régale est égal à 1/2000. A une telle dilution, le verre n'est pas attaqué et il est facile de masquer le fluor restant.

Mode opératoire: On pèse 100 mg de zirconium sous forme de copeaux que l'on place dans un bécher Phillips de 100 ml en ajoutant 20 ml d'eau régale et 10 gouttes d'acide fluorhydrique 1/5. On ajoute 2 ml de la solution de ^{60}Co de marquage dont l'activité a été au préalable déterminée à l'aide du compteur à scintillation. On recouvre d'un verre de montre et porte à ébullition, en rajoutant si nécessaire, un peu d'eau régale de temps à autre jusqu'à dissolution. Lorsque celle-ci est complète, on ajoute environ 0.1 g de chlorure d'aluminium pour complexer les ions fluor, puis on évapore la plus grande partie de la solution. Il faut éviter une évaporation à sec qui favorise l'adsorption du cobalt sur les parois et rend difficile la remise en solution de la prise. Lorsqu'il ne reste que quelques ml de solution dans le bécher, on rajoute 10 ml d'acide chlorhydrique concentré et on évapore à nouveau presque complètement. On reprend finalement par 20 ml d'une solution de HCl 9 *N*, de manière à pouvoir ensuite effectuer directement le passage sur les colonnes échangeurs d'ions.

Séparation

Lorsque la solution 9 *N*, obtenue après attaque selon le processus décrit au paragraphe précédent, est introduite dans une colonne chromatographique contenant de la résine Dowex 1-X8, le cobalt (ainsi qu'un certain nombre d'autres cations tels que Fe, Cu, Zn, etc.) se fixe sous forme d'anions complexes. L'adjonction de HCl 4 *N* détruit le complexe du cobalt qui se trouve alors élué seul. La solution obtenue, pratiquement exempte de cations étrangers, contient cependant des traces de résine qui deviennent gênantes lorsqu'il s'agit de la détermination de très petites quantités de cobalt. On effectue alors une purification par extraction au moyen d'une solution éthérée de dithizone. Après minéralisation de l'extrait, le dosage du cobalt s'effectue dans les meilleures conditions possibles.

Mode opératoire: (*a*) On prépare les colonnes chromatographiques de la manière suivante: Laver plusieurs fois une quantité suffisante de résine Dowex avec HCl 0.01 *N*, en éliminant les particules trop fines par décantation. Placer cette résine dans des colonnes de 6 mm de diamètre intérieur, entre deux tampons de laine de verre, de manière à obtenir une hauteur de 120 mm environ, effectuer un lavage final en laissant écouler, à travers les colonnes, 30 ml de HCl 0.01 *N*. On sature ensuite par 5 ml de HCl 9 *N*. La vitesse de passage des solutions doit être de l'ordre de 1 ml par minute.

(*b*) On introduit dans une colonne la solution chlorhydrique 9 *N* contenant le zirconium. Après écoulement complet, on lave par 20 ml de HCl 9 *N*. On élue ensuite

le cobalt avec 25 ml de HCl 4 *N*. Les pertes de cobalt au cours de cette opération sont de l'ordre de 2 à 3%.

(*c*) On ajoute à la solution, du citrate de sodium afin que la concentration de celui-ci soit de 10% (soit 2.5 g pour un volume de 25 ml). On amène au pH d'environ 8.2 à l'aide d'une solution concentrée, puis d'hydroxyde de sodium 1 *N*. On transvase dans une ampoule à décanter de 100 ml et extrait par 5 ml d'une solution à 0.05% de dithizone dans l'éther en agitant énergiquement durant 2 min. On recommence cette dernière opération jusqu'à ce que la dithizone conserve sa couleur verte (deux extractions sont suffisantes dans le cas présent). On lave finalement la solution aqueuse avec 5 ml d'éther pur. Les solutions éthérées renfermant le dithizonate de cobalt sont recueillies dans une ampoule à décanter, on élimine la solution aqueuse entraînée et on lave avec 2 ml de HCl 0.1 *N*. On laisse écouler la solution organique dans une capsule de pyrex et on évapore à sec.

(*d*) La minéralisation du dithizonate de cobalt doit être conduite avec soin car c'est elle qui peut être responsable des plus grandes pertes. On effectue une attaque préalable du résidu avec 1 ml d'acide nitrique et on évapore à sec au moyen d'une calotte chauffante. On ajoute ensuite 5 ml d'acide perchlorique, recouvre la capsule d'un verre de montre suffisamment creux contenant de l'eau pour favoriser la condensation des vapeurs d'acide et place le tout sur une plaque chauffante (à environ 250–280°) jusqu'à décoloration complète, ce qui nécessite environ 2 heures. On enlève alors le verre de montre et ajoute 2 ml de chlorure de sodium (ou KCl) 0.1 *M* (charge destinée à prévenir les adsorptions sur le verre), puis on évapore sous calotte chauffante. On reprend par 1 ml d'acide chlorhydrique concentré et évapore à nouveau pour détruire le perchlorate alcalin formé. On ajoute finalement 2 ou 3 ml d'eau bidistillée et évapore pour chasser les dernières traces d'acide. Le résidu final, qui doit être tout à fait blanc, est repris quantitativement par 2 ml d'eau bidistillée et transvasé dans une petite éprouvette; on en mesure l'activité à l'aide du compteur à scintillation.

Détermination spectrophotométrique

La solution contenant le cobalt (ainsi que le support ajouté au cours de la minéralisation) ne renferme pratiquement plus d'ions étrangers et la détermination spectrophotométrique peut être faite avec précision. On forme le complexe en présence de nitroso-sel R et mesure la densité optique à 520 mμ. La méthode a été décrite en détails lors d'un article précédent[5], aussi n'en donnerons nous qu'un bref résumé.

Mode opératoire: (*a*) La solution à analyser (2 ml) est transvasée dans un tube à centrifuger jaugé de 5 ml en y ajoutant 2 ml de solution tampon acétique de pH 6. On introduit ensuite 0.5 ml de solution aqueuse de nitroso-sel R.

(*b*) On développe la coloration en chauffant durant 60 sec au bain-marie bouillant, puis on introduit 0.5 ml d'acide nitrique concentré et continue à chauffer durant 30 sec pour détruire l'excès de réactif.

(*c*) Après refroidissement sous un courant d'eau, on ajuste éventuellement au trait de jauge, puis on centrifuge durant 15 min à environ 3000 t/m pour éliminer toute trace de matière en suspension qui pourrait fausser la mesure spectrophotométrique.

(*d*) On introduit la solution dans une cuve colorimétrique de 10 mm et on mesure l'extinction à 520 mμ par rapport à un essai témoin préparé dans les mêmes conditions.

On effectue dans les mêmes conditions une série de contrôle (voir page 56) afin d'éliminer tout risque d'erreur.

Interprétation des résultats

L'extinction ayant été déterminée, on se reportera aux essais témoins — (a), (b) et (c), page 56 ou à une courbe d'étalonnage[5] — pour calculer la quantité de cobalt présente. On déduit de la valeur trouvée la quantité de cobalt introduite par les réactifs — (d), page 56 — et la solution de marquage et on effectue une correction pour tenir compte des pertes survenues en cours d'analyse. Ces pertes sont déterminées avec précision par le rapport des comptages initiaux (page 57) et finals (page 58). La stabilité du compteur à scintillation est contrôlée par une source étalon lors de chaque série de mesure.

Résultats du dosage du cobalt dans le zirconium RG.SG.101

Le dosage a été conduit selon la méthode décrite et les résultats trouvés sont donnés dans les Tableaux I et II.

TABLEAU I

DOSAGE SPECTROPHOTOMÉTRIQUE DU COBALT DANS LE ZIRCONIUM RG.SG.101

(volume lors de la détermination = 5 ml)

Prises (mg)	*Marquage au ^{60}Co*			*Densité optique*	*Co trouvé[a] (µg)*	*Teneur en cobalt (%)*
	Initial (c.p.m.)	*Final (c.p.m.)*	*Pertes (%)*			
100	39827	31708	20.4	0.01255	0.314	0.00031
100	40243	35733	11.2	0.01402	0.315	0.00032
100	40988	34104	16.8	0.01157	0.277	0.00028
100	40438	35020	13.4	0.01260	0.290	0.00029
100	40339	33117	17.9	0.01309	0.318	0.00032
100	39405	35076	11.0	0.01348	0.302	0.00030
100	39875	29670	25.6	0.01162	0.312	0.00031
100	40134	36804	8.3	0.01260	0.273	0.00027

[a] Compte tenu des pertes et déduction faite du cobalt de marquage (0.007 µg)

TABLEAU II

DOSAGE SPECTROPHOTOMÉTRIQUE DU COBALT DANS LE ZIRCONIUM RG.SG.101
AVEC CONTRÔLE PAR ADJONCTION D'UNE QUANTITÉ CONNUE DE COBALT (étalon interne)

Prises (mg)	*Marquage au ^{60}Co*			*Co ajouté (µg)*	*Densité optique*	*Co trouvé[a] (µg)*	*Teneur en Co (%)*
	Initial (c.p.m.)	*Final (c.p.m.)*	*Pertes (%)*				
100	40211	34177	15.0	—	0.01407	0.331	0.00033
100	39120	33685	13.9	0.290	0.02564	0.600	0.00031
100	40314	33782	16.2	0.490	0.03358	0.810	0.00032

[a] Compte tenu des pertes et déduction faite du cobalt de marquage (0.007 µg)

La valeur moyenne établie sur les 11 résultats précédents est de 0.000305%, l'écart standard étant de $\pm 0.000005_6\%$. La limite de confiance calculée pour une probabilité de 95% est de $\pm 0.000012_4\%$. La teneur en cobalt du zirconium RG.SG.101 est donc comprise entre 0.000293 et 0.000318%.

DISCUSSION

Le procédé de séparation et de dosage qui a été décrit peut être appliqué même si l'on ne dispose pas des instruments et des produits qui permettent le marquage par

isotopes radioactifs. Si l'on travaille dans les conditions indiquées, on constate que les pertes moyennes (contrôlées sur un grand nombre d'essais[6]) survenant en cours d'analyse sont de l'ordre de 15%. On devra donc multiplier les résultats obtenus par le facteur 1.176.

Mais si la méthode des traceurs est applicable avec le matériel de laboratoire dont on dispose, une simplification notable du processus général de séparation est possible. On procèdera alors de la manière suivante:

Au cours de l'élution du cobalt à l'aide d'acide chlorhydrique 4 *N*, on recueillera la solution par fractions successives de 2 ml environ. Une détermination rapide d'activité permettra alors de choisir 1 ou 2 fractions contenant la plus grande partie du cobalt. La portion d'éluat ainsi sélectionnée (2 à 4 ml au lieu de 25 ml) ne contient qu'extrêmement peu de résidus gênants provenant de la résine Dowex et une purification par extraction au moyen de dithizone devient inutile. Après avoir chassé l'acide chlorhydrique par évaporation, on reprend par 2 ml d'eau bidistillée et effectue la détermination spectrophotométrique de la manière habituelle (voir page 58).

La durée moyenne d'un dosage, qui est de 10 h environ en suivant la méthode décrite, se réduit à 6 h en suivant le processus de séparation simplifié.

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RÉSUMÉ

Une étude a été faite concernant la séparation et le dosage du cobalt d'une prise de 100 mg de „zirconium reactor-grade". La séparation est faite à l'aide de résine Dowex 1-X8 et le cobalt, après élution, est purifié par extraction par la dithizone. On dose le cobalt séparé par spectrophotométrie au moyen de nitroso-sel R. La méthode est contrôlée par l'emploi d'un traceur radioactif (^{60}Co). Une teneur de 0.0003% de Co est déterminée avec une précision de ± 4%.

SUMMARY

A method is described for the separation and determination of cobalt in 100 mg reactor-grade zirconium. Separation is effected by means of an ion-exchange resin. After elution, the cobalt is purified by extraction with dithizone and determined spectrophotometrically with the help of nitroso-R-salt. With this method a content of 0.0003% can be determined with an accuracy of ± 4%.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Abtrennung und Bestimmung von Kobalt in 100 mg Zirkonium-Reaktormaterial. Die Abtrennung erfolgt mit einem Austauscherharz, die Reinigung über den Dithizonkomplex und die Bestimmung spektrophotometrisch mit Hilfe des Nitroso-R-Salzes. Ein Gehalt von 0.0003% kann nach dieser Methode mit einer Genauigkeit von ± 4% erfasst werden.

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DETERMINATION OF HIGHER MOLECULAR WEIGHT ALIPHATIC ALDEHYDES AND KETONES

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Several spectrophotometric methods have been developed for formaldehyde[1-5], for total aliphatic aldehydes and ketones[5-7], total aliphatic aldehydes[8-10] and ketones[11]. In all of these methods the first members of the series, formaldehyde and acetone, have more intense absorption spectra than the remaining members of the series. The available data suggest that formaldehyde or acetone is the most prominent of the individual carbonyl compounds present in combustion gases[12,13] or smog[14]. An analytical procedure capable of detecting and determining higher molecular weight aldehydes or ketones in the presence of formaldehyde or acetone would provide an additional means of studying the composition of carbonyl compounds in such mixtures.

In developing a new spectrophotometric method for diolefins[15], it was found that formaldehyde, acetaldehyde and acetone were quite unreactive with the reagents used. However, propionaldehyde, acrolein, butanone and higher molecular weight aldehydes and ketones did react to form products with fairly intense absorption bands. In addition to absorption maxima in the 380 to 395 mμ range possessed by both the aldehydes and the ketones, the straight-chain aldehydes have absorption maxima or shoulders in the 440 to 465 mμ region. Most alkanediones react to form intense absorption maxima in the 380 to 390 mμ region.

EXPERIMENTAL PROCEDURE

The aldehyde or ketone is dissolved in 2-methoxyethanol containing 25% concentrated (85%) phosphoric acid. This solution is reacted in the ratio of 8 parts of sample solution to 2 parts of reagent, a 2% solution of *p*-nitrobenzenediazonium fluoborate in 2-methoxyethanol. Since the reagent decomposes slowly on standing, it should be prepared on the day of use.

The sample and reagent are allowed to react for four hours at 35°. The spectra then are measured on a Cary Model 11 or equivalent spectrophotometer using cells that provide an optical path length of 1 cm.

RESULTS

Aldehydes and ketones

Some preliminary absorbance measurements were made on solutions containing 1.8% of the *p*-nitrobenzenediazonium reagent. However, this procedure results in lower

sensitivities, and the reagent blank is more highly colored and less stable than those resulting from use of solutions containing only 0.4% reagent. The solutions containing a 0.4% reagent concentration react for 4 h at 35° (Table I).

TABLE I

ABSORPTION SPECTRA OF REACTION PRODUCTS FORMED BETWEEN *p*-NITROBENZENEDIAZONIUM FLUOBORATE AND ALDEHYDE OR KETONES

Aldehyde or ketone	*1.8% reagent concentration*[a,b]		*0.4% reagent concentration*[a,c]	
	λmax, mμ	K_{spec}, μg^{-1} ml cm^{-1} [d]	*λmax, mμ*	K_{spec}, μg^{-1} ml cm^{-1} [d]
formaldehyde	470–480	0.000002	465	0.00005
acetaldehyde	420	0.0001	380	0.00089 ± 0.00013[e]
	465	0.00008	450	0.00035 ± 0.00006
propionaldehyde	400	0.001	390	0.035 ± 0.007
	450	0.0015	440	0.024 ± 0.001
butanal	—	—	385	0.017 ± 0.001
			440 sh	0.012 ± 0.002
2-methyl-propanal	—	—	390	0.081 ± 0.005
pentanal	—	—	387	0.021 ± 0.003
3-methyl-butanal	—	—	395	0.021 ± 0.001
acrolein	—	—	387	0.03[f]
2-butenal	450	0.003	390	0.016 ± 0.002
2-methyl-2-butenal	—	—	385	0.013 ± 0.003
			500 sh	0.002
acetone	400	0.0003	380	0.002
butanone	410	0.004	383	0.036 ± 0.003
3-pentanone	—	—	380	0.022 ± 0.003
3-methyl-2-butanone	—	—	392	0.051 ± 0.003
2,3-butanedione	—	—	390	0.0015
2,4-pentanedione	—	—	380	0.22 ± 0.04
1,2-cyclo-hexanedione	—	—	383	0.20

[a] Reagent concentration in final solution after addition of reagent to sample solution.
[b] 4-h reaction period at room temperature.
[c] 4-h reaction period at 35°.
[d] Specific absorption coefficient, absorbance per μg of aldehyde or ketone in each ml of initial sample solution.
[e] Standard deviation.
[f] At 20 μg, absorbance not linear with concentration.

All of the aldehydes and ketones except formaldehyde form products with absorption maxima in the 380–395 mμ range. However, the intensities of the products of the acetaldehyde, acetone, and 2,3-butanedione with *p*-nitrobenzenediazonium fluoborate are 0.1–0.01 of the products formed by the higher molecular weight aldehydes and ketones. The absorbances were found to be linear with concentration, at least in the 5 to 50 μg/ml range, for the higher molecular weight compounds.

All of the straight-chain aldehydes used gave indications of a second absorption band in the 440–465 mμ region. The reaction product of the formaldehyde possesses only one band at 465 mμ. In the acetaldehyde product this band intensifies somewhat and is shifted about 15 mμ towards the ultraviolet, while a second band appears at 380 mμ. In the propionaldehyde product the higher wavelength band greatly increases in intensity and shifts another 10 mμ towards the ultraviolet. The overlap

between this higher wavelength band and the intensified lower wavelength band, now peaking at 390 mμ, is such as to make the 440-mμ absorption appear as weak maximum or as a shoulder. The reaction product formed by the butanal also has a shoulder at about 440 mμ. The pentanal product shows only a slight inflection in the 430–440 mμ region. Consequently, the higher wavelength absorption band becomes indistinguishable under the lower wavelength band as the molecular weight of straight-chain aldehyde increases. The intensities at 440 mμ are linear with concentration in the 5 to 50 μg/ml range for propionaldehyde, butanal and pentanal. The absorbance also is a linear function of concentration for acetaldehyde at 450 mμ in the 500 to 3000 μg/ml range.

The unsaturated straight-chain aldehydes, acrolein and crotonaldehyde, do not have a similar higher wavelength band appearing in the absorption spectra of their reaction products. The 2-methyl-2-butenal reaction product does show a shoulder at 500 mμ in addition to the usual lower wavelength absorption band.

The substitution of an isopropyl group for an *n*-propyl group, or correspondingly, a methine for the methylene group alpha to the carbonyl group of an aldehyde or ketone, results in an appreciable increase in intensity and a small shift towards the visible of the absorption bands of the reaction products. This effect is clearly shown by comparing the absorption bands of the products formed by methylpropanal and 3-methyl-2-butanone with the corresponding bands of the products formed by butanal and 3-pentanone.

The presence in a ketone of two carbonyl groups either adjacent or separated by a methylene group also results in a large increase in intensity of the absorption bands of the reaction products. For example, the reaction product formed by 2,4-pentanedione has ten times as intense an absorption band as does 3-pentanone, and over one hundred times as intense a band as does butanedione.

Interferences

It has been reported elsewhere[15] that some conjugated diolefins, and many phenols, couple with *p*-nitrobenzenediazonium fluoborate in phosphoric acid–2-methoxyethanol to form products absorbing in the 400 mμ region. Phenol, *p*-cresol, almost all monolefins, other classes of hydrocarbons and nitrogen oxides interfere only to a small or negligible extent[15]. Benzaldehyde reacts very slightly, if at all, with the diazonium salt.

Analysis of liquid mixtures

One of the applications suggested by the data given in Table I is the analysis of one or more higher aldehydes such as propionaldehyde in mixtures also containing formaldehyde, acetaldehyde or acetone. Formaldehyde, acetaldehyde and acetone have small or negligible absorption in the 440–460 mμ range. Consequently, three liquid mixtures were analyzed. Two of these mixtures contained formaldehyde in large excess, acetaldehyde and propionaldehyde. The third mixture contained formaldehyde in large excess, acetone and propionaldehyde. All three of these mixtures reacted to produce absorption maxima at 456 mμ and a second maximum at 375–380 mμ. Both of these types of maxima are shifted away from the positions of the wavelength maxima in reagent solutions containing only propionaldehyde (Table I). The composition of these mixtures and the calculated concentrations using both 440 and

456 mμ as the analytical wavelengths are given in Table II. The compositions are calculated from the absorptivities for propionaldehyde alone at 440 and 456 mμ.

The calculated concentrations of propionaldehyde are in fair agreement with the actual concentrations. However, the concentration values obtained using 440 mμ as the analytical wavelength are 5% to 10% low, whereas the values obtained using 456 mμ as the analytical wavelength are 5% to 10% high. If 450 mμ were used as the analytical wavelength, the calculated and actual propionaldehyde concentrations would be in good agreement. However, the choice of 450 mμ is an arbitrary one and this wavelength might be less satisfactory for mixtures in a different concentration range or with other components present.

TABLE II

ANALYSIS OF LIQUID MIXTURES OF ALIPHATIC ALDEHYDES AND KETONES FOR PROPIONALDEHYDE

Mixture	*Conc. μg/ml*	*Calculated conc. μg/ml of propionaldehyde*[a]	
		440 mμ	*456 mμ*
formaldehyde	945		
acetaldehyde	48	32	39
propionaldehyde	35.7		
formaldehyde	945		
acetaldehyde	48	44	49
propionaldehyde	45.4		
formaldehyde	945		
acetone	41	41	47
propionaldehyde	45.0		

[a] 4-h reaction period at 35°

DISCUSSION

The present method would appear to be applicable to the analysis of total straight-chain aldehydes in the three to five carbon atom range in mixtures also containing formaldehyde, acetaldehyde, and acetone. The reaction products formed by higher molecular weight branched-chain aldehydes and the four carbon and higher ketones also will absorb appreciably in the 440 to 460 mμ range. The specific absorptivities of the products in the 440 mμ region vary from about 0.005 μg^{-1} ml cm^{-1} for 3-pentanone to 0.03 μg^{-1} ml cm^{-1} for 2-methylpropanal. However, most of the absorptivities at 440 mμ are in the 0.01 to 0.02 μg^{-1} ml cm^{-1} range. This wavelength region might be useful for a quantitative estimation of total higher molecular weight aldehydes and ketones in oxygenate mixtures.

The maxima in the 380- to 395-mμ region are most intense (Table I), but vary over a six-fold range (even excluding the diones). These maxima are more subject to interference by phenols and diolefins than are the absorption maxima in the 440- to 460-mμ range. Consequently, except for very simple mixtures, or possibly in mixtures containing appreciable quantities of 2,4-pentanedione or related diones, the 380- to 395-mμ region appears to be of limited analytical applicability.

The products formed by most of the higher molecular weight aldehydes and ketones do not appear to be *p*-nitrophenylhydrazones formed by direct attack of the diazo-

nium cation on the carbonyl group. Formaldehyde, acetaldehyde, acetone, 2,3-butanedione and benzaldehyde all form very weakly absorbing products. If the *p*-nitrophenylhydrazones of these carbonyl compounds are formed, the products should have about as intense absorption spectra as the other aldehydes and ketones. Consequently, the position of attack must be at the methylene or methine carbon atom alpha to the carbonyl group, and carbonyl compounds lacking such activated carbon-to-hydrogen bonds react only to a small extent with the diazonium compound.

The formation of the phenylhydrazones of triones have been reported when diazonium salts have been reacted with several diones including 2,4-pentanedione, 1,2-cyclopentanedione, 1,3-cyclohexanedione, etc.[16]. These may be the type of products formed by the 2,4-pentanedione and 1,2-cyclohexanedione in the solvent system used in the present investigation.

Aldehydes and ketones with activated carbon-to-hydrocarbon bonds also will react to form formazans with diazonium salts[16]. However, such reactions usually procede readily in an alkaline rather than in acidic medium[16]. However, the formation of formazans from simple aldehydes and ketones recently have been reported in acidic media[17] by reacting phenylhydrazines and an oxidant with the carbonyl compound or by reacting phenylhydrazines and a diazonium salt with the carbonyl compound. Propionaldehyde, butanone, acrolein and the higher molecular weight members of these series of oxygenated compounds also may be forming the corresponding formazans under the experimental conditions of this study.

The interpretation of the results reported here is somewhat complicated by the second absorption band formed in the reactions of straight-chain aldehydes. The presence of two band systems suggest that two types of reaction products may be formed from these compounds.

SUMMARY

The visible absorption spectra have been measured for the reaction products formed by aldehydes and ketones with *p*-nitrobenzenediazonium fluoborate in a phosphoric acid-2-methoxyethanol solvent medium. The absorption maxima for the reaction products of higher molecular weight aldehydes and ketones are much more intense than those formed by formaldehyde, acetaldehyde and acetone. This intensity effect has been used to analyze for propionaldehyde in mixtures also containing formaldehyde, acetaldehyde or acetone. The nature of the reaction products are considered.

RÉSUMÉ

Une méthode est proposée pour le dosage des aldéhydes et des cétones. Elle consiste à mesurer le spectre d'absorption de leur produit de réaction avec le fluoborate de *p*-nitrobenzènediazonium, en milieu acide phosphorique–méthoxyéthanol.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung höher molekularer Aldehyde und Ketone. Sie beruht auf der Messung der Absorptionsspektren der Reaktionsprodukte mit *p*-Nitrobenzoldiazonium-fluoborat in einem Gemisch von Phosphorsäure und 2-Methoxy-äthanol als Lösungsmittel.

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A METHOD FOR THE DETERMINATION OF STARCH IN WOOD

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INTRODUCTION

In order to follow the process of starch resorption in fire-damaged and insect-defoliated eucalyptus trees it was necessary, as a first step, to devise a method of determining starch in large numbers of wood samples which was rapid, specific and sufficiently accurate to show starch variation in trees sampled at monthly intervals. The accurate determination of starch in wood has been a matter of some difficulty brought about mainly by the low concentration of starch normally present and the fact that it has common solubility properties with other polysaccharides occurring in wood. SCHORGER[1] reviewing work in this field found that the methods then in use involved either acid or enzyme hydrolysis and used dilute acid or hot water to isolate the starch. CAMPBELL[2] obtained results on English oak and Walnut wood by taka-diastase hydrolysis which were two to three times higher than were found on the same material by hot water extraction. GIBBS[3] also used takadiastase with only moderate success to determine starch in the twigs of *Betula populifolia*. NIELSEN AND GLEASON[4] used perchloric acid to disperse starch in small samples of fresh plant material and finally determined the starch by iodine spectrophotometry. This method, suitably modified, seemed most likely to provide useful results.

EXPERIMENTAL

Apparatus

All absorption measurements were made with a Unicam SP 500 Spectrophotometer using a tungsten filament lamp and 1-cm glass absorption cells.

Preparation of sample

The material for analysis was prepared by grinding the transverse cross-sectional face of a piece of sapwood with a disc-sander, passing the ground material through

a 200-mesh sieve (B.S.S.) and drying it for three days in a desiccator over concentrated sulphuric acid. Experiments have shown that the transverse cross-sectional face is the best surface of the sample to use since it provides material, which is truly representative of the piece of wood being analysed, in a state which ensures that all the starch is dissolved. Material from tangential and radial faces contains some of the starch grains enclosed within cell walls which are not attacked by perchloric acid.

Procedure

Weigh approximately 0.4 g of material and transfer it to a 50-ml beaker. Add 4.7 ml of 7.2 *M* perchloric acid and allow to react for 10 min with occasional stirring. Transfer the contents of the beaker to a 50-ml volumetric flask and bring to volume. After centrifuging, place a 10-ml aliquot in a 50-ml volumetric flask together with a drop of phenolphthalein and make alkaline with 2 *N* sodium hydroxide. Add 2 *N* acetic acid until the colour is discharged and then add a further 2.5 ml followed by 0.5 ml 10% w/v potassium iodide and 5 ml 0.01 *N* potassium iodate. Allow the colour to develop for 15 min, bring to volume and measure the absorption at 650 mμ using a blank prepared without starch as zero. Repeat samples having more than 3% starch using smaller portions.

RESULTS AND DISCUSSION

Replicate analyses

Two series of six replications were carried out on one sample of 200-mesh wood to test the reproducibility of the method. A mean result of 3.25% was obtained with a standard deviation of 0.08%.

Effect of strength of perchloric acid

Equal weights of the same sample of ground wood were treated as above except that various strengths of perchloric acid were employed (Table I). 7.2 *M* perchloric acid was adopted for use in all subsequent analyses.

TABLE I

Acid strength (M)	*Optical density*	*Acid strength (M)*	*Optical density*
4.8	0.093	9.6	0.116
6.0	0.110	10.8	0.074
7.2	0.123	12.0	0.010
8.4	0.122		

Effect of time of contact with 7.2 M perchloric acid

Equal weights of ground wood were treated as above except that they were left in contact with the perchloric acid for varying periods (Table II).

TABLE II

Time of contact (min)	*Optical density*	*Time of contact (min)*	*Optical density*
5	0.272	20	0.288
10	0.293	25	0.272
15	0.287	30	0.277

It was decided that 10 min should be allowed for reaction between the starch and perchloric acid though it is evident that for up to 30 min the method is not very sensitive to this variable.

Size of aliquot in final solution

As its preparation is time consuming it was desirable to use as small a sample of wood as possible without sacrificing accuracy. For most samples it was found that 0.2 g wood did not provide a sufficient concentration of starch for a 5-ml aliquot to be used. Accordingly an experiment using a 25-ml aliquot was carried out. The results were very similar for both 5-ml and 25-ml aliquots though the greater dilution caused by the larger aliquot so retarded the reaction rate that the maximum optical density was not reached for several hours. Also, because of the necessity to restrict the volume to about 40 ml, strong alkali was needed in the neutralisation of the aliquot. Another experiment using 0.4 g of wood and 5- and 10-ml aliquots was carried out. From the results there was little to choose between them but because the larger aliquot gave a higher optical density it was decided that a sample of 0.4 g and an aliquot of 10 ml would be standardised upon. (Table III).

TABLE III

Weight of sample g	*Aliquot ml*	*Optical density*
0.4018	5	0.117
0.4018	10	0.262
0.4020	5	0.133
0.4020	10	0.254

Standard reference curve

A standard reference curve was set up using A.R. potato starch. Accurately weighed quantities of starch ranging from 0.0057 g to 0.04 g were weighed and treated according to the procedure given above*. The optical density was plotted against the weight of the starch corrected to zero moisture content. The moisture content was determined by heating a sample of the starch for 4 h at 105° and 25 mm Hg and measuring the loss of weight after cooling over phosphorus pentoxide in a desiccator[5].

Because the method depends ultimately on the reaction of the amylose in the starch with iodine it was desirable to determine the amylose contained in the wood starch. This was done by comparing wood starch with A.R. potato starch, using both polarimetry and iodine-spectrophotometry. Three difficulties presented themselves in the polarimetric method when applied to the starch in wood.

(*1*) The calcium chloride solution is frequently so strongly coloured by tannins, etc. that optical rotation cannot be read.

(*2*) Other optically active water-soluble constituents may be present.

(*3*) Owing to the small amount of starch present the rotation is very low.

These difficulties were overcome by preparing a starch-enriched sample of wood in the following way: A large piece of the sapwood of a New Guinea species of Crypto-

* 5-ml aliquots were taken and diluted to 10 ml with water before the other reagents were added.

carya was reduced to sawdust and successive 200-g portions were stirred with about 2 to 3 l of water for 30 min each then filtered through a small pad of glass wool. The liquor volume was kept constant by the addition of more water as each new portion of sawdust was added to it. Next the liquor was left to stand and the supernatent solution removed. The residual material was washed through a 200-mesh sieve (B.S.S.) with cold water, centrifuged and dried under vacuum at room temperature. This process removed any optically active and colouring compounds present and provided a sample with a greater rotating power.

Known weights of this material and of A.R. potato starch were dispersed in $CaCl_2$ solutions and the starch content of each calculated from polarimeter measurements[6]. Since this measurement is independent of the amount of amylose in the starch it was taken as the actual starch content of the material.

Using the same solutions, the starch levels were then determined by the method given by KERR[7]. Aliquots of the potato starch solution were treated by the perchloric acid method. From the information obtained a reference curve was established (Fig. 1).

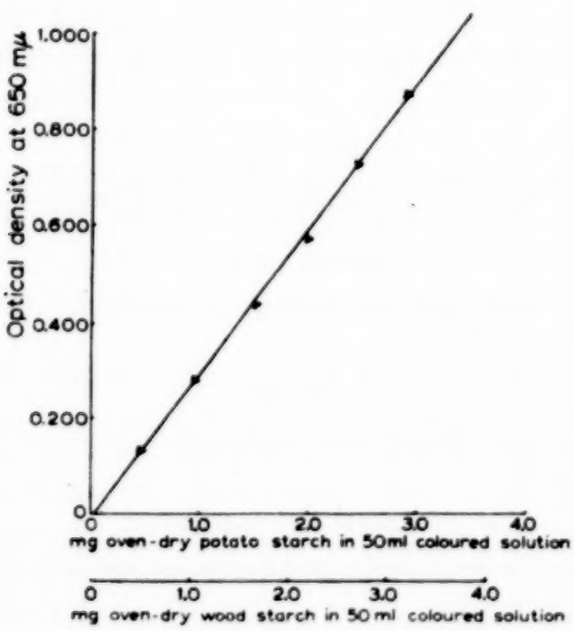

Fig. 1.

In order to calculate the amylose in wood starch from this data one final piece of information was required, namely, the amylose content of the potato starch. The figure chosen from among the many estimates made by various workers was 25.5% obtained by KERR AND TRUBELL[8]. BATES, FRENCH AND RUNDLE[9] have stated that, judged on the basis of the fraction which takes up the most iodine "KERR's crystalline amylose is the best of the amylose fractions yet prepared" and "that it is also the amylose fraction which has been subject to the most careful refractionation, and the one showing the best crystalline properties".

Starch content of wood material by optical rotation = 21.2%

Starch content of wood material by iodine-spectrophotometry = 19.3%

$$\text{Therefore amylose in wood starch} = \frac{19.3}{21.2} \cdot \frac{25.5}{1} = 23.2\%$$

This value was used in all subsequent determinations of starch in wood. The data used for the reference curve together with the corresponding weights of wood starch obtained by application of a factor, 1.10 (25.5/23.2) are given in Table IV.

TABLE IV

Weight of moisture-free potato starch in 50 ml coloured solution mg	*Optical density at 650 mμ* (y)	*Corresponding weight of moisture-free wood starch in 50 ml coloured solution* (x) mg
0.00	0.000	0.00
0.46	0.130	0.51
0.95	0.279	1.05
1.50	0.433	1.65
1.97	0.575	2.17
2.44	0.728	2.68
2.89	0.870	3.18

$$y = 0.2719x - 0.008$$

Therefore if a 10-ml aliquot is taken from the original perchloric acid solution, starch in wood

$$= \left(\frac{1839(y + 0.008)}{\text{Moisture-free weight of sample in mg}}\right) \%$$

SUMMARY

A rapid and simple method of estimating starch in wood is described which is suitable for carrying out large numbers of determinations.

RÉSUMÉ

Une méthode rapide et simple est décrite pour le dosage de l'amidon dans le bois. Ce procédé convient à des analyses en série.

ZUSAMMENFASSUNG

Beschreibung einer für Serienbestimmungen geeigneten schnellen und einfachen Methode zur Bestimmung von Stärke in Holz.

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THE DETERMINATION OF LEAD IN COPPER-BASE ALLOYS AND STEEL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

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INTRODUCTION

There are at least three methods available for determining lead in copper-base alloys. One of these, a volumetric procedure based on precipitation of lead chromate by an excess of potassium dichromate and titration of the excess reagent with a standard ammonium ferrous sulphate solution, is rapid and is frequently used in routine control laboratories. The method is applicable to a wide range of samples but, unless very careful attention is given to detail, erroneous results are obtained.

A direct reading spectrometric method is available, using either a Hilger 3-m Polychromator or a Hilger direct reading attachment to a medium spectrograph[1]. This procedure is also rapid but limited to samples available in a special form and regular calibration of the instrument, using similar samples of known lead content, is necessary.

These two procedures are in current use in industrial laboratories and there is also available, for referee work, a gravimetric method[2] based on an initial electrodeposition of lead peroxide and subsequent conversion of the recovered deposit to lead molybdate. This method is accurate but time-consuming; a single determination takes about a day to complete. It is permissible to weigh the lead peroxide (*i.e.* the increase in weight of the anode) and calculate the lead content of the sample using an empirical factor, but results obtained in this way are of doubtful accuracy, especially when the weight of deposit exceeds about 10 mg.

A rapid routine control procedure which is accurate and independent of sample form was, therefore, desirable and in view of our earlier successful work with atomic absorptiometric methods[3], it was decided to investigate possible applications of this new analytical technique to the determination of lead in copper-base materials. This was the main objective of the experimental work subsequently described, but when this part of the work was completed it seemed that, with only simple modification, the procedure could be used for the direct determination of lead in steels and, through the courtesy of The British Iron and Steel Research Association, the samples referred to in Table VI were kindly supplied.

A method currently used for determining lead in steels[4] is based on solution of the sample in hydrochloric acid, precipitation of lead as sulphide and subsequent conversion of the recovered lead precipitate to lead molybdate and weighing as such. This method is accurate but involves the use of hydrogen sulphide and a single determination takes at least 2 h to complete.

APPARATUS

The apparatus used was the same as that described by GIDLEY AND JONES[3]. A sealed-off hollow cathode lamp was made with a cathode machined from a solid piece of leaded brass containing about 3.5% of lead. The lamp consisted of a 250-ml round-bottom flask with a quartz window sealed across the neck with black wax. The electrodes were sealed into the lamp by using waxed cone and socket joints, for ease of replacement; the lamp was evacuated, filled with argon and processed in a manner similar to that described by JONES AND WALSH[5]. (A running life of at least 250 h has been achieved using this type of lamp). With this lamp it was possible to use a direct indication method for measuring intensity, which is simpler and more rapid than the integration method used earlier[3].

EXPERIMENTAL

The most suitable line for absorption measurements was found to be Pb 2833.1 Å, but at low operating currents both the line intensity and line to background intensity ratio were low, resulting in negligible absorption when solutions containing 100 μg lead/ml were examined. Using higher currents both line intensity and line to background intensity ratios increased and corresponding absorptions also increased. Maximum absorption occurred when the lamp was operated at the maximum output current (50 mA) of the stabilised power supply but, under these conditions, the lamp became overheated and a compromise operating current (40 mA) was used for all subsequent work. Table I shows absorptions obtained with varying operating currents.

TABLE I

EFFECT OF HOLLOW CATHODE LAMP CURRENT ON ABSORPTION

Lamp current mA	*Optical density due to 100 μg lead/ml*
10	—
20	0.075
30	0.176
40	0.220
45	0.232
50	0.232

In order to reduce the effect due to continuous background radiation, a minimum monochromator slit width is necessary and, in addition, it is essential to use a narrow slit to separate the absorbed line (2833 Å) from two other emission lines at 2824 Å and 2840 Å which are not absorbed. Insufficient intensity was available to allow the narrowest available slit width to be used, and a width of 0.1 mm was shown to be the best compromise.

A calibration curve relating optical density and concentration, covering the range 0–200 μg lead/ml in an aqueous solution, showed a slight curvature towards the concentration axis. An optical density of 0.22 was obtained using a 100-μg lead/ml standard, with a limit of detection of 2 μg lead/ml, based on an arbitrary detection limit of an optical density of 0.005 (approximately 1% absorption).

Acids normally used for the dissolution of lead-bearing metallurgical samples were tested to establish their effect, if any, on absorption. Solutions (1 + 9) of nitric,

hydrochloric, perchloric and fluoboric acids were separately examined, each in the presence of 50 μg lead/ml, and very little interference was noted, as shown by results in Table II.

TABLE II

EFFECT OF ACIDS ON THE DETERMINATION OF LEAD

(50 μg lead/ml added)

Acid[a]	*μg lead/ml found*
Nitric	46.0
Hydrochloric	46.0
Perchloric	48.0
Fluoboric	46.0

[a] Normal laboratory reagent acids diluted (1 + 9)

The slight interference is probably due to the increased viscosity of the acid solution which reduces the rate at which the solution is atomised, with a consequent reduction in absorption. This, however, can be compensated for by adding the same volume of acid to the standard solution.

The effects of several elements, particularly those likely to be present in either alloying or trace amounts in non-ferrous materials normally analysed for lead, were examined separately for possible interferences. To a solution containing 50 μg lead/ml was added a solution containing 1000 μg/ml (a ratio of 20 : 1) of one of the following elements: sodium, calcium, copper, aluminium, magnesium, iron, nickel, tin, zinc, and silicon and, apart from the possible viscosity effect, none of these elements interfered (Table III).

TABLE III

EFFECT OF VARIOUS ELEMENTS ON THE DETERMINATION OF LEAD

(50 μg lead/ml in the presence of 1000 μg/ml of a second element)

Element added	*μg lead/ml found*
Sodium	49.5
Calcium	50.0
Copper	47.0
Aluminium	47.0
Magnesium	50.0
Iron	48.0
Nickel	50.0
Tin	48.3
Zinc	49.8
Silicon	50.0

It was expected that some elements which form refractory oxides, *e.g.* aluminium and silicon, might seriously interfere, but no such interference was observed.

Typical samples were analysed using a tentative procedure based on the experimental work so far described. A convenient weight of the sample, sufficient to give a final solution containing about 100 μg lead/ml, was dissolved in nitric acid containing

hydrochloric acid to inhibit precipitation of metastannic acid. The sample solution and a suitable standard solution were then atomised and optical densities were determined. The standard solution contained an *amount of copper* equivalent to the *weight of sample* in the test solution, to compensate for any viscosity effect caused by the presence of a high concentration of other elements.

The procedure was applied to several lead-bearing copper alloys, and results obtained (Table IV) compared very favourably with those obtained by the lead molybdate procedure[2].

TABLE IV

DETERMINATION OF LEAD IN COPPER ALLOYS

Sample	*Lead (%)*			
	Chemical		*Atomic absorption*	
B.C.S. Standard No. 183 Bronze A	1.83[a]		1.81	1.81
B.C.S. Standard No. 179 Manganese Brass B	0.78[a]		0.77	0.79
B.C.S. Standard No. 207 Bronze C	0.41[a]		0.41	0.42
I.C.I. Reference Standard Brass No. 7	3.55		3.52	3.55
Leaded Brass XR.2	1.77	1.78	1.77	1.77
Leaded Brass XR.4	1.02	1.03	1.02	1.01
Leaded Brass XR.11	2.10	2.14	2.13	2.14
Leaded Brass XR.38	0.37	0.38	0.39	0.40
Leaded Brass XR.39	3.19	3.19	3.19	3.20

[a] Certificate value

From a series of tests on leaded brass samples, it was established that the lead content of a single sample could be made available by one person within 20 min of receipt of the sample turnings, and two analysts could complete 50 similar samples in a normal working day of 8 h.

The method was also used for a routine check on results obtained on control samples of leaded brass, using the direct reading attachment[1]. In these tests, involving more than 100 determinations, over the range 2.5–4.0% lead, the standard deviation of the differences between spectrometric and atomic absorption results was 0.06%. As the direct reading spectrometric method is only reproducible to 0.05%, this indicated that a high degree of calibration has been maintained for that instrument and a good accuracy for the atomic absorption procedure is implied.

Reproducibility of the method is controlled mainly by the uncertainty of the absorption measurement and, in a normal determination, the mean of from five to ten measurements is taken to improve the precision. From the range of individual measurements, an indication of reproducibility can be obtained. Based on a series of more than twenty determinations at the 100-μg lead/ml level, the reproducibility of measurement for a single test was calculated to be about 2%, expressed as a coefficient of variation.

To establish the accuracy of the proposed method for determining lead in complex copper alloys, British Chemical Standard No. 183/1, containing about 85% copper, 5% tin, 5% zinc and 3.5% lead, was analysed. A reference solution was also prepared containing, in about the same proportions, all the elements known to be present in

the standard; the amount of metallic lead used in preparing this solution was weighed accurately. Absorption due to lead, using the standard and sample solutions independently, was measured twenty times for each solution; the procedure was also repeated three times on independently weighed samples of the standard alloy. Results obtained are shown in Table V. When the lead values obtained by atomic absorption are compared with the reference solution, an accuracy of about 0.025%, expressed as a standard deviation, is indicated.

TABLE V

DETERMINATION OF LEAD IN B.C.S. NO. 183/1

Lead (%)	
Proposed B.S.I. method[a]	*Atomic absorption*
3.44	3.38
3.46	3.39
3.49	3.41

[a] Preliminary separation of lead electrolytically, followed by conversion to, and weighing as, lead molybdate.

The possibility of determining lead in steels was not considered until after the method for copper-base alloys had been fully developed. It appeared, however, that only a few preliminary tests would be necessary in order to establish the validity of the method when applied to the examination of typical steels.

Six steel samples were kindly supplied, together with their established lead contents, by The British Iron and Steel Research Association. These samples had been extensively examined by the Pig Iron, Carbon and Low Alloy Steels Analysis Sub-Committee in the development of a referee gravimetric lead method[4]. Later, a further sample, 'X', was supplied by the Chairman of the same Sub-Committee (Mr. S. W. CRAVEN), following a request for a similar steel sample with an established lead content, to be disclosed to the authors only after the lead content had been determined by the proposed atomic absorption procedure. The samples were dissolved in hydrochloric acid, oxidised with nitric acid, atomised etc., and the lead contents evaluated from the relationship between optical densities resulting from test solutions and a

TABLE VI

DETERMINATION OF LEAD IN LEADED STEELS

Sample	*Lead (%)*		
	Chemical[a]	*Atomic absorption*	
MGS/163	0.280	0.277	0.287
MGS/196A	0.175	0.182	0.185
MGS/257A	0.076	0.080	0.070
MGS/195	0.175	0.185	
MGS/272	0.115	0.125	
MGS/274	0.185	0.195	
X	0.280[b]	0.282	0.280

[a] Preliminary separation of lead as sulphide, followed by conversion to, and weighing as, lead molybdate.

[b] Result supplied by Mr. S. W. CRAVEN; others (chemical) by B.I.S.R.A.

solution containing pure iron and pure lead. Results of these tests are shown in Table VI and all are in good agreement.

METHOD I. DETERMINATION OF LEAD IN COPPER-BASE ALLOYS

(0.05–5% Pb)

Equipment

Hilger atomic absorption attachment, H.909, to Uvispek spectrophotometer, H.700, fitted with photomultiplier detection.

Special solutions

Acid mixture: To about 300 ml of water add 300 ml of nitric acid ($d = 1.42$). Add 200 ml of hydrochloric acid ($d = 1.18$), cool and dilute to 1 l.

Standard lead solution: Weigh, as accurately as possible, 0.5 g of pure lead (*e.g.* British Chemical Standard No. 210b) and dissolve in the minimum volume of nitric acid (1 + 1). Cool and dilute to 1 l.

1 ml ≡ 0.5 mg lead.

Standard copper/lead solution A: Dissolve 10.00 g of high purity copper in 100 ml of the acid mixture. Cool, add 200.0 ml of the standard lead solution and dilute to 1 l.

1 ml ≡ 100 μg lead.

Standard copper/lead solution B: Dissolve 5.00 g of high purity copper in 50 ml of the acid mixture. Cool, add 200.0 ml of the standard lead solution and dilute to 1 l.

1 ml ≡ 100 μg lead.

Preparation of mean standard curve

To each of 5 100-ml calibrated flasks add, separately, 5.0, 10.0, 20.0, 30.0, and 40.0 ml of the standard lead solution and dilute each to the mark. These solutions contain 25, 50, 100, 150 and 200 μg lead/ml respectively.

Instrument settings, using a leaded brass hollow cathode lamp, are as follows: lamp current, 40 mA; atomiser air pressure, 15 lb/sq.in.; wavelength, 2833 Å; photomultiplier voltage, 1100 V; slit width, 0.10 mm.

Switch on the hollow cathode lamp, light the burner and switch on the constant voltage supply to the photomultiplier tube. Allow 1 h for emission from the lamp to reach a constant value.

With no light entering the monochromator, adjust the galvanometer to zero. With light from the lamp entering the monochromator, adjust the wavelength control until a peak intensity is indicated by the galvanometer.

Spray water through the atomiser, bring the galvanometer to zero, by means of the voltage dividing potentiometer, and take the reading (R_0), which is proportional to the light intensity falling on the photomultiplier. Spray each of the standard lead solutions, taking the reading (R) at the zero point each time. Repeat the series of tests five times. Prepare two more calibration curves in the same manner.

Calculate the optical density for each standard solution (optical density = log R_0/R). Scale each curve to an optical density of 0.220 for 100 μg lead/ml. Take the average readings for each of the three curves and plot these as the final mean standard curve.

TABLE VII

RECOMMENDED SAMPLE WEIGHT AND VOLUME OF ACID MIXTURE

Lead content (%)	*Sample (g)*	*Acid mixture (ml)*
0.1–1.0	1.0	10
1.0–3.5	0.5	5

Procedure

Dissolve the recommended weight of sample in the appropriate volume of acid mixture, boil, to expel nitrous fumes, cool and dilute to 100 ml in a calibrated flask.

Determine the optical density of the sample solution as described under *Preparation of mean standard curve*. Determine the optical density of the appropriate standard copper/lead solution in conjunction with each batch of samples, *i.e.* solution A for 1-g samples and solution B for 0.5-g samples (Note).

Scale the optical density of the standard solution to 0.220 and correct optical densities of sample solutions proportionally. Read off the amount of lead in the sample solution by reference to the mean standard curve and calculate the percentage of lead in the sample.

Note

The appropriate standard solution corresponding to the sample weight must be used to compensate for any variation in viscosity of the solutions. The use of distilled water in all dilutions is implied throughout.

METHOD 2. DETERMINATION OF LEAD IN STEELS
(0.05–0.5% Pb)

Equipment

See Method 1.

Special solutions

Standard lead solution: 1 ml ≡ 0.5 mg lead. See Method 1.

Standard iron solution: Dissolve 2.00 g of high purity iron (*e.g.* H.H.P. iron) in 20 ml of hydrochloric acid ($d = 1.18$) and oxidise with 1–2 ml of nitric acid ($d = 1.42$). Cool and dilute to 100 ml.

Standard iron/lead solution: Dissolve 2.00 g of high purity iron in 20 ml of hydrochloric acid ($d = 1.18$) and oxidise with 1–2 ml of nitric acid ($d = 1.42$). Add 10 ml of standard lead solution and dilute to 100 ml.

1 ml ≡ 50 μg lead (0.25% lead in iron).

Procedure

Dissolve 2.00 g of the sample in 20 ml of hydrochloric acid ($d = 1.18$) and oxidise with 1–2 ml of nitric acid ($d = 1.42$). Dilute and filter off any precipitated silica, wash the filter thoroughly with warm water and dilute the cooled filtrate to 100 ml.

Use the same instrument settings and setting up procedure as described under *Preparation of mean standard curve* in Method 1 and determine the optical density of the standard and sample solutions. Draw a calibration curve through the points

obtained for the two standard iron solutions, read off the amount of lead in the sample solution by reference to this curve and calculate the percentage of lead in the sample.

CONCLUSION

Atomic absorption spectrophotometry provides a simple, rapid and accurate procedure for determining lead in copper-base alloys and leaded steels. Because of its freedom from inter-element interference, there is no reason to doubt that the method could be applied to the determination of lead in other materials, *e.g.* highly alloyed steels.

ACKNOWLEDGEMENTS

Acknowledgements are made to The British Iron and Steel Research Association for supplying the steel samples and for permission to quote the results obtained by the Methods of Analysis Sub-Committee, and to Messrs. J. M. JACOBS and A. NICHOLLS for their helpful suggestions and experimental work in connection with the development of these procedures.

SUMMARY

The principle of atomic absorption spectrophotometry has only recently been exploited as an analytical technique and details are given of the development of a procedure for determining lead in copper-base alloys and leaded steels. The recommended method is simple, rapid and provides results as accurate as those obtained by the more time-consuming alternative methods in current use.

RÉSUMÉ

Une méthode est proposée pour le dosage du plomb dans des alliages à base de cuivre et dans des aciers, au moyen de la nouvelle technique de spectrophotométrie par absorption atomique. Le procédé recommandé est simple, rapide et donne des résultats aussi précis que ceux obtenus avec les méthodes habituelles.

ZUSAMMENFASSUNG

Beschreibung einer einfachen, raschen und genauen Methode zur Bestimmung von Blei in Kupferlegierungen und Stählen. Sie beruht auf der neuen Technik der Spektrophotometrie durch atomare Absorption.

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CONDUCTOMETRIC TITRATION OF METAL ACETATES IN AQUEOUS MEDIUM

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Methods for acid–base potentiometric titrations of metal acetates in nonaqueous medium have been recently reported. CASEY AND STARKE[1] titrated 18 metal acetates in glacial acetic acid using perchloric acid as a titrant; this method was unsuccessful for the acetates of copper, tin, antimony, bismuth and uranium which were not dissociated in that solvent. CUNDIFF AND MARKUNAS[2] titrated the acetates of copper, nickel and uranium by an indirect method which involved acidification of the salt with an excess of sulphuric acid, addition of a nonaqueous solvent and differential potentiometric titration; obviously this procedure gives the amount of the acetate ion, while the cation amount can be deduced only if there is a stoichiometric ratio between them. DAS AND PALIT[3] titrated the acetates of calcium, cadmium, magnesium, zinc, lead and mercury using perchloric and hydrochloric acids as titrants.

Conductometric analysis has found wide application in the precipitation titrations of metal salts, while replacement titration with acids seems to have been applied only to alkali metals; thus sodium acetate titration with hydrochloric acid has been reported[4], while titrations of less electro-positive metal acetates are not known.

A recent finding in these laboratories has shown that weak organic bases, having ionization constants down to 10^{-12}, could be conductometrically titrated with trichloroacetic acid, following solution in an excess of aqueous acetic acid[5]. As this procedure is equivalent to the titration of an organic base acetate in the presence of an excess of acetic acid, we took into consideration the possibility of applying this method to the titration of metal acetates in aqueous medium.

The graph relating to the conductometric titration with a strong acid of a metal acetate, shows a first straight line corresponding to the conductance variation due to the replacement of the anion CH_3COO^- by the titrant anion; the former combines with the hydrogen ion of the titrant. After the equivalence point the conductance increases sharply as a consequence of the rapid increment of free hydrogen ions. Therefore in the titration curve of a given acetate, the sharpness of the equivalence point angle depends on the values of the ionization constant and of the anionic mobility of the titrant.

Trichloroacetic acid, being a strong acid ($K_A = 2 \cdot 10^{-1}$) and having an anionic mobility ($\lambda^\circ_{25} = 35.0$) lower than that of the acetic acid ($\lambda^\circ_{25} = 40.9$), seemed particularly suitable as titrant. The equilibrium

$$CH_3COOH + H_2O \leftrightharpoons CH_3COO^- + H_3O^+$$

existing with the equilibrium

$$CH_3COOMe \leftrightharpoons CH_3COO^- + Me^+$$

contributes to the curvature near the equivalence point without shifting it. Therefore it is possible to use an excess of acetic acid when this increases the salt solubility; this excess, which in the case of titrations of organic bases improves the sharpness of the end-point angle, in the case of the metal acetates exerts a practically negligible influence on the slope of the first straight line.

This method can also be applied to the titration of metal salts of acids weaker than acetic (*e.g.* carbonates) by dissolving them in an excess of aqueous acetic acid, as well as to salts of acids stronger than acetic if they can be transformed into acetates (*e.g.* nitrates).

EXPERIMENTAL

Apparatus

Resistance measurements were carried out using two alternating current Wheat stone bridges. The first bridge was as previously described[6]. The second one, which was constructed in our laboratories, was supplied by a very low distortion sinusoidal generator through an insulation transformer. Balance point zero readings were made on a cathode-ray tube through a tuned amplifier. Its operative characteristics were frequency 1000 hertz; bridge supply 0.5 V r.m.s.; sensitivity 0.1 ‰. It was equipped with an oil bath maintained at the working temperature $\pm 0.01°$.

A modified Jones and Bollinger cell[6] was used. The electrodes consisted of two discs of platinized platinum (diameter 2.3 cm) facing each other at a distance of 16.2 cm.

The automatic-filling microburet had a capacity of 5 ml with 0.01-ml graduations.

Reagents and procedure

Metal acetates were of C.P., or better, grade and were titrated as received, with the exception of sodium and potassium acetates which were previously dried.

A 2-*N* solution of trichloroacetic acid was obtained by dissolving chromatography grade trichloroacetic acid in distilled water and standardizing the solution conductometrically against anhydrous sodium acetate. Alternatively the acid was standardized with sodium carbonate using bromophenol blue as indicator.

Samples of acetates corresponding to 2–6 mmoles were dissolved in 40–50 ml of water or 50% water–ethanol mixtures. The titrations were carried out in a nitrogen atmosphere at about 22°. The measured resistance value were between 800 and 20000 ohms. The reciprocals of the measured resistance values were corrected for volume variations.

Analyses

The accuracy of the method was checked by analysis of each salt by conventional quantitative techniques. The acetates of sodium and potassium used were of AnalaR standard and therefore only required to be dried at 120° for 2 h.

The analytical method used: (*a*) Ammonium bicarbonate was treated with a strong base to liberate ammonia which was absorbed by an excess of acid. (*b*) Lithium, strontium and barium were determined as sulphates. (*c*) Calcium as oxide. (*d*) Magnesium, manganese and zinc as pyrophosphates. (*e*) Cadmium as the 2-(*o*-hydroxy-

phenyl)-benzoxazole complex. (*f*) Cobalt as the pyridine thiocyanate complex. (*g*) Silver as chloride. (*h*) Copper as thiocyanate. (*i*) Nickel as the dimethylglyoxime complex. (*j*) Uranium as the hydroxyquinoline complex.

RESULTS AND DISCUSSION

The titration curve of a metal acetate shows a rounding in the vicinity of the equivalence point, due to the trichloroacetate hydrolysis. This does not affect the intersection point location when the acetate of a monovalent metal is titrated (Fig. 1), but in the case of a bivalent metal this rounding hinders the location of the straight line corresponding to the weakest stage, and the end-points are not well defined.

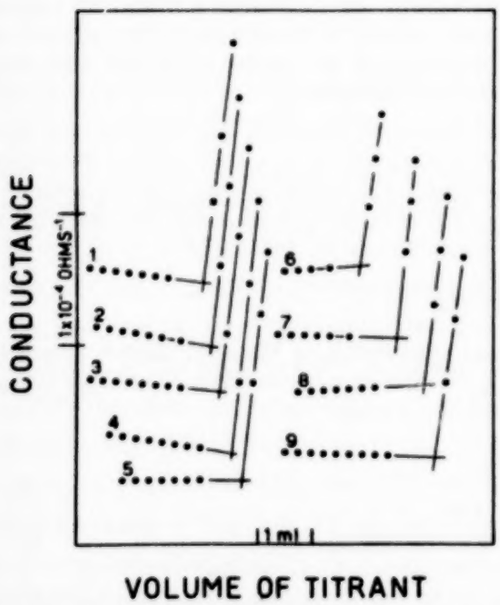

Fig. 1. Conductometric titration of metal acetates in aqueous medium with 2 *N* trichloroacetic acid. 1. Sodium; 2. Potassium; 3. Lithium; 4. Ammonium*; 5. Magnesium; 6. Silver; 7. Strontium; 8. Calcium; 9. Barium.

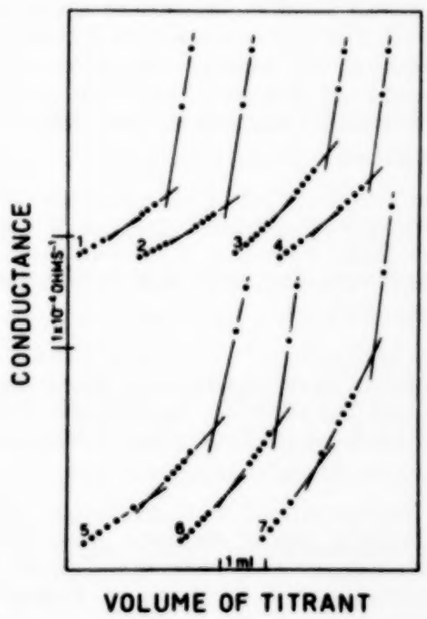

Fig. 2. Conductometric titration of metal acetates in 50% water–ethyl alcohol with 2 *N* trichloroacetic acid. 1. Nickel; 2. Manganese; 3. Cadmium; 4. Cobalt; 5. Uranium; 6. Zinc; 7. Copper.

This difficulty can be overcome by using as solvent a 50% water–ethanol mixture. Ethanol decreases hydrolysis enabling the second straight line to be obtained, but also decreases dissociation of the salt, which results in more obtuse end-point angles.

In Fig. 2 the curves show very obtuse angles at the first equivalence point. At the second end-point, they are more obtuse than those obtained in absence of ethanol (Fig. 1), but are sharp enough to allow a good accuracy.

Acetates of lithium, sodium, potassium, magnesium, calcium, strontium, barium, copper, silver, zinc, cadmium, uranium, manganese, cobalt and nickel were examined by the proposed method and all recoveries were in close agreement with the purity established by alternative analytical methods.

Ammonium bicarbonate was titrated following solution of the sample in an excess of aqueous acetic acid.

The acetates of iron, mercury and aluminium could not be titrated because their

* 0.4 g of ammonium bicarbonate dissolved in 40 ml of water containing 0.35 g acetic acid.

hydroxides or basic salts precipitated by hydrolysis were insoluble even in the presence of an excess of acetic acid. Chromium acetate gave a completely curved titration line. Lead acetate did not give a straight neutralization line, although it is a salt of a relatively strong base ($pK_B = 7.3$), probably owing to its small dissociation. Silver acetate was completely dissolved after a small addition of titrant.

For each compound examined, from two to four conductometric determinations were carried out. From the values obtained by this method a standard deviation of 0.3% was calculated. The value of the systematic error is negligible when compared with its standard deviation (Systematic error $= -0.13 \pm 0.64\%$).

SUMMARY

Fifteen metal acetates in aqueous medium have been conductometrically titrated with trichloroacetic acid. The method has been applied to the titration of mono- and bivalent metals and angles at the equivalence point are sharp enough to allow accurate results to be obtained. Metal salts of acids weaker than acetic can be determined following solution in an excess of acetic acid and titration, because the weaker acid which is displaced does not interfere.

RÉSUMÉ

Une méthode est proposée pour le titrage conductométrique d'acétates métalliques, au moyen de l'acide trichloracétique. Les sels d'acides plus faibles que l'acide acétique peuvent être également titrés, après dissolution dans l'acide acétique en excès.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von ein- und zweiwertigen Metallen durch konduktometrische Titration der Acetate mit Trichloressigsäure. Salze von schwächeren Säuren als Essigsäure können durch Zusatz von Essigsäure ebenfalls titriert werden.

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AMPEROMETRIC ARGENTIMETRIC AND MERCURIMETRIC TITRATION OF SULFHYDRYL

I. ARGENTIMETRIC TITRATION

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The amperometric argentimetric titration of sulfhydryl in unsubstituted mercaptans was introduced by KOLTHOFF AND HARRIS[1] using a rotating platinum wire electrode (R.Pt.W.E.) as indicator electrode. Titrations were carried out in 60–70% alcohol in ammonia buffers, to make chloride harmless. The accuracy of the method was reported to be 0.3% with amounts of 2 mg mercaptan sulfur per 100 ml and 1–2% with amounts of 0.2 mg mercaptan sulfur. The above procedure was applied without essential change by BENESCH AND BENESCH[2] to the determination of sulfhydryl groups in amino acids and proteins. Generally they used solutions of high alcohol content (90%). Results were reported: for thioglycolic acid, 98 ± 4% (0.09–0.46 mg/30 ml), for cysteine HCl, 102.5 ± 1.2% (0.162 mg/30 ml) and for glutathione (reduced), 97.7 ± 2.7%. Working in 93% ethanol and using an ammonia buffer of pH 10.4, SARKER AND SIVARAMAN[3] claim that 2–4 mg of cysteine could be determined with an accuracy of 0.4%.

The argentimetric determination of cysteine and cystine in aqueous solutions with ammonia buffer (0.2–0.3 *M* in NH_4NO_3, 0.1 *M* in NH_3 was studied by KOLTHOFF AND STRICKS[4]. They found that silver cysteinate (RSAg) can react with an excess of silver; this reaction is slow and they recommend that the titrations be carried out very rapidly. It was also noticed that close to the equivalence point RSAg is measurably dissociated into silver ions. This, combined with the fact that RSAg can react with an excess of silver (*vide infra*), may be the reason why several authors observed that a considerable excess of silver is present at the graphically located amperometric end-point. Thus, STAIB AND TURBA[5] report that at the end-point the molar ratio of cysteine and silver is 1 : 1.35. SLUYTERMAN[6] carried out titrations in an ammonia buffer of pH 9.1 and also in a "tris" buffer of pH 7.7. This buffer, which is composed of tris(hydroxymethyl)aminoethane and its salt was introduced by BENESCH *et al.*[7] for the titration of sulfhydryl in proteins. SLUYTERMAN reported the following results in an ammonia buffer of pH 9.1 (a) and in a tris buffer of pH 7.7 (b): cysteine, 133 ± 3% (a) and 155 ± 3% (b); glutathione, 92 ± 2% (a) and 98 ± 1% (b); cysteine ethyl ester, 108 ± 2% (a) and 143 ± 4% (b); thioglycolic acid, 132 ± 3% (a) and 136 ± 3% (b). In Table I are compared the results obtained by BURTON[8] with those by other authors in the titration of cysteine (RSH) and glutathione (GSH).

The large errors obtained in the titration of cysteine must be attributed to the fact that the reaction between RSH and silver can give rise to the formation of a host of

TABLE I

RESULTS BY VARIOUS AUTHORS OBTAINED WITH CYSTEINE (RSH) AND GLUTATHIONE (GSH)

Results refer to 100% pure products

Compound	*Author*	*Medium*	*Buffer*	*pH*	*End-point %*	*End-point % (Burton[8])*
RSH	BENESCH AND BENESCH[2]	alcohol	ammonia	10.0	102.5	145
RSH	SARKER AND SIVARAMAN[3]	alcohol	ammonia	10.4	99.7	119
RSH	SLUYTERMAN[6]	water	ammonia	9.1	133	142
RSH	SLUYTERMAN[6]	water	tris	7.7	155	146
GSH	BENESCH AND BENESCH[2]	alcohol	ammonia	10.0	95–100.4	90
GSH	SLUYTERMAN[6]	water	ammonia	9.1	92	100
GSH	INGRAM[9]	water	ammonia	9.2	≏100	100
GSH	BENESCH *et al.*[7]	water	tris	7.4	98	130

complexes as was shown by KOLTHOFF AND STRICKS in unpublished work[10]. Argentimetric potentiometric titration curves of cysteine[10] also indicate that RSAg reacts with excess of silver. The titrations were carried out with different initial concentrations of cysteine (in ammonia buffers of varying pH) using a silver electrode as indicator electrode. From the large number of results it appeared that at pH smaller than 8.4 the formation of RSAg is favored, while at higher pH several other complexes were formed. Dependent on the specific conditions under which the potentiometric titrations were carried out end-points were found where the excess of silver varied between 10 and 50%. Evidence for the formation of the following complexes, $(RSAg)_{10}Ag^+$, $(RSAg)_4Ag^+$ and $(RSAg)_2Ag^+$, respectively was presented. Also in the potentiometric titration of thioglycolic acid silver complexes of varying composition were found. The above conclusions were substantiated by extensive polarographic studies with the dropping mercury electrode. When the ratio of RSH to Ag^+ was greater than one, a complex $RSAg \cdot RSH$ (or $[Ag(RS)_2]^-$) was found. The anodic cysteine wave became equal to zero before the attainment of the equivalence point (RSAg). After this point the diffusion current of the silver ammine ion was found to be less than corresponds to the stoichiometric excess of silver, the amount of silver bound by RSAg could be calculated from this difference.

Solubility measurements[10] of RSAg in a borax buffer in the presence of varying concentrations of silver nitrate showed that one silver ion combines with 4RSAg when the concentration of silver nitrate is less than 10^{-3} *M* and with 3RSAg when this concentration is greater than 10^{-3} *M*. The saturated solution of RSAg was colorless but became yellow with an excess of silver. Altogether it appeared that the system $RSAg-Ag^+$ is quite complex.

CECIL AND MCPHEE[11] studied the potentiometric titration of cysteine and glutathione at various pH. In the pH range between 2.5 and 7.5 they found at the end-point 17% more silver bound than corresponds to RSAg. At pH less than 1.7 glutathione bound an amount of silver about 30% in excess to GSAg.

From this review it appears that the results of an amperometric argentimetric titration of a substituted mercaptan may be considerably in error. It appeared desirable to investigate this titration under different conditions with some substituted mercaptans in order to find which group or groups are responsible for the error in the titration and to find means to reduce the error. In a subsequent paper ampero-

metric titrations with mercuric chloride and nitrate respectively are described. Mercury mercaptides are much more stable than the silver mercaptides.

EXPERIMENTAL

Materials used

Silver nitrate was a Mallinckrodt analytical reagent. A 0.1-*M* stock solution of silver nitrate was standardized against pure sodium chloride. The stock solution was kept in a dark bottle and dilutions were prepared daily.

Sodium sulfite was a Mallinckrodt A.R. product. A 1-*M* oxygen-free stock solution was kept in a refrigerator. The titer was determined iodometrically. Diluted sulfite solutions were prepared daily under air-free conditions.

Cystine was a Merck reagent grade product which had been recrystallized and dried in vacuo at 70°. A stock solution was prepared which was 0.01 *M* in cystine and 0.1 *M* in nitric acid.

Cysteine was a Mann product. An air-free 0.1-*M* stock solution of cysteine in 0.2 *N* nitric acid was prepared and kept in a refrigerator. The titer was checked frequently by titrations with ferricyanide[14]. During a period of two months no change in the titer was found.

Cysteine hydrochloride: two products were used, one from Merck, which contained 2% water and the other from Brother, which contained 9.24% water. The sulfhydryl content was determined by LAVINE's iodometric procedure[12] and by the ferricyanide method[14]. Amperometric mercurimetric titrations to be described in a subsequent paper gave results which agreed within 1% with those obtained by the ferricyanide procedure, while the iodometric procedure gave results which were 2% high.

Glutathione (GSH) was an Eastman product which had been dried in vacuo at 70°. A 0.01-*M* stock solution was prepared under air-free conditions.

Pure thioglycolic acid (TSH) was obtained by distillation at reduced pressure (in nitrogen atmosphere) of an Eastman product. The stock solution was prepared from the fraction boiling between 95–100° at about 6 mm Hg.

Pure colorless 2-mercaptoethanol (ESH) was obtained by double distillation in vacuo of a technical product from Union Carbon Co. Dilute solutions of ESH and TSH were prepared daily from 0.1-*M* stock solutions and kept at ice temperature.

All other reagents were of reagent grade. Conductivity water has been used throughout.

Experimental methods

Current-potential curves were determined and amperometric titrations carried out using a manual apparatus[13]. The platinum wire electrode was rotated at a constant speed of 1800 r.p.m. Potentials are reported *vs.* the saturated calomel electrode (S.C.E.). A saturated KCl–agar salt bridge was used in experiments carried out in the presence of chloride and a saturated KNO_3–agar salt bridge in the absence of chloride. Most of the titrations were carried out with 50 ml deaerated solution in a 100-ml beaker. The nitrogen used was a Linde product which was bubbled through two wash bottles containing a chromium(II) solution and water respectively. For the deaeration of solutions buffered with ammonia buffers the nitrogen was then passed through two wash bottles containing the same buffer. Reagent was added from a 1-ml Guilmont type microburette. Titrations of cysteine were carried out with a silver-

coated platinum electrode. The electrode was daily cleaned with hot nitric acid (1 : 1) and coated with silver at —0.3 V for 10 min at a current of about 20 μA in an ammonia buffer of pH about 9. Between titrations the electrode was wiped between two fingers and washed with a stream of water. The titrations of other mercaptans were carried out using an uncoated platinum electrode which was cleaned after each experiment with concentrated nitric acid.

RESULTS

Titration of cysteine in ammonia and tris buffers

Titrations were carried out in an ammonia buffer of pH 9.05 or in 0.133 M tris buffer acidified with nitric acid to give a pH 7.4. Current-potential curves obtained in mixtures of 10^{-4} M RSH and varying excess of silver showed that the diffusion current of the excess of silver is not proportional to the concentration of the silver ammine ions in excess over RSAg. After addition of 30% excess of silver only a very small diffusion current was observed. On further addition of silver the diffusion current of the silver ammine ions increased rapidly. The results of amperometric titrations with solutions which were $2.5 \cdot 10^{-5}$ M to $4 \cdot 10^{-4}$ M in RSH at an applied potential of —0.3 V *vs.* SCE are reported in Table II. At cysteine concentrations less than 10^{-4} M

TABLE II

TITRATION OF CYSTEINE WITH $AgNO_3$ IN 50 ml 0.1 M AMMONIUM NITRATE–AMMONIA BUFFER pH 9.05. $E_{applied} = -0.3$ V

Molarity of RSH	*$AgNO_3$ used*		*mg RSH*		*Error* %	*Alcohol* %
	ml	*Molarity*	*Taken*	*Found*		
$2.5 \cdot 10^{-5}$	0.665	$2.5 \cdot 10^{-3}$	0.152	0.201	+33	—
$5 \cdot 10^{-5}$	0.670	$5 \cdot 10^{-3}$	0.303	0.406	+34	—
$7.5 \cdot 10^{-5}$	1.010	$5 \cdot 10^{-3}$	0.454	0.611	+35	—
10^{-4}	1.35	$5 \cdot 10^{-3}$	0.606	0.832	+35	—
$2 \cdot 10^{-4}$	0.720	$2 \cdot 10^{-2}$	1.211	1.745	+44	—
$4 \cdot 10^{-4}$	0.600	$5 \cdot 10^{-2}$	2.423	3.63	+50	—
$6 \cdot 10^{-5}$	0.385	10^{-2}	0.364	0.468	+28	70
$9 \cdot 10^{-5}$	0.585	10^{-2}	0.546	0.710	+30	70
$1.6 \cdot 10^{-4}$	1.125	10^{-2}	0.971	1.363	+41	70
$2.4 \cdot 10^{-4}$	0.865	$2 \cdot 10^{-2}$	1.455	2.10	+44	70
$6 \cdot 10^{-5}$	0.365	10^{-2}	0.364	0.444	+22	86
$9 \cdot 10^{-5}$	0.550	10^{-2}	0.546	0.668	+23	86
$1.6 \cdot 10^{-4}$	1.040	10^{-2}	0.971	1.262	+30	86
$2.4 \cdot 10^{-4}$	0.830	$2 \cdot 10^{-2}$	1.455	2.013	+38	86

the error was constant and equal to +34% in aqueous medium, +30% in 70% alcohol and +23% in 86% alcohol. The error was found to increase at higher cysteine concentrations. Similar results were found in titrations of cystine after quantitative reduction with sodium amalgam. From a few examples of titration lines given in Fig. 1 it is clear that part of the silver added after the equivalence point (RSAg) is bound until about 30% after the end-point, when the excess reagent line is found. The error is reduced when the titrations are carried out in an ammonia buffer in the presence of 0.1 M sodium sulfite. For example in the titration of 2.5, 5, 10 and $20 \cdot 10^{-5}$ M

cysteine (or cystine) the errors were —2%, 0%, +15% and 20% respectively. In the presence of sulfite part of the ammino silver ions are transformed into complex sulfite ions which seem to be less reactive toward RSAg than the ammino silver ions are.

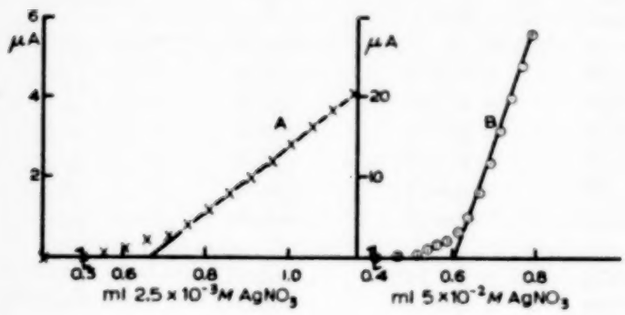

Fig. 1. Titration lines of cysteine in ammonia buffer, pH 9.05 at —0.3 V *vs.* SCE. A. $2.5 \cdot 10^{-5}$ *M* RSH; B. $4 \cdot 10^{-4}$ *M* RSH. ⌒ indicates equivalence point [RSAg].

TABLE III

TITRATIONS IN TRIS BUFFER AT THE R.Pt.W.E.

Applied potential: —0.1 V

Molarity of RSH	*$AgNO_3$ used*		*mg RSH*		*Error* %	*Alcohol* %
	ml	*Molarity*	*Taken*	*Found*		
$4 \cdot 10^{-5}$	0.27	10^{-2}	0.242	0.327	+35	—
$8 \cdot 10^{-5}$	0.57	10^{-2}	0.485	0.690	+42	—
$1.6 \cdot 10^{-4}$	1.14	10^{-2}	0.971	1.380	+42	—
$4 \cdot 10^{-5}$	0.315	10^{-2}	0.242	0.380	+57	70
$8 \cdot 10^{-5}$	0.625	10^{-2}	0.485	0.757	+56	70

Titrations carried out in buffer solutions which were 0.133 *M* in tris (pH 7.4) gave higher results than those obtained in ammoniacal buffers containing the same amount of cysteine. Some results are given in Table III. While in ammonia buffers the error decreased in the presence of 70% alcohol, the opposite effect was observed in the tris buffers where the error increased markedly. For example in the titration of $4 \cdot 10^{-5}$ *M* cysteine in aqueous medium the error was +35% as compared to 57% in 70% alcoholic medium.

Titration of glutathione (GSH)

As is evident from Table IV good results are obtained in this titration over the wide concentration range between $5 \cdot 10^{-5}$ *M* to $2 \cdot 10^{-3}$ *M* glutathione. Sulfite has no effect and the titration is very suitable for the determination of oxidized glutathione.

Thioglycolic acid (TSH)

Thioglycolic acid behaves toward silver similarly to cysteine. Current-potential curves in solutions $2 \cdot 10^{-4}$ *M* in TSH, 0.25 *M* in ammonium nitrate and 0.1 *M* in ammonia, containing various amounts of silver nitrate, showed that part of the silver in excess over TSAg is bound. Titrations carried out with solutions $2 \cdot 10^{-4}$ *M* to $2 \cdot 10^{-3}$ *M* in TSH yielded end-points which were 20–34% higher than corresponds to

TABLE IV

TITRATION OF GLUTATHIONE IN AMMONIA BUFFER 0.25 *M* IN AMMONIUM NITRATE AND 0.1 *M* IN AMMONIA

$E_{applied} = -0.3$ V

Molarity of GSH	*$AgNO_3$ used*		*mg GSH*		*Error %*	*Addition*
	ml	*Molarity*	*Taken*	*Found*		
$5 \cdot 10^{-5}$	0.245	10^{-2}	0.768	0.783	−2.0	
10^{-4}	0.250	$2 \cdot 10^{-2}$	1.536	1.536	0.0	
$2 \cdot 10^{-4}$	0.495	$2 \cdot 10^{-2}$	3.073	3.104	−1.0	
$4 \cdot 10^{-4}$	1.00	$2 \cdot 10^{-2}$	6.146	6.146	0.0	
10^{-3}	0.490	10^{-1}	15.366	15.673	−2.0	
$2 \cdot 10^{-3}$	1.010	10^{-1}	30.732	31.039	+1.0	
$2 \cdot 10^{-4}$	0.490	$2 \cdot 10^{-2}$	3.073	3.134	−2.0	0.1 *M* Na_2SO_3
$4 \cdot 10^{-4}$	0.985	$2 \cdot 10^{-2}$	6.146	6.238	−1.5	0.1 *M* Na_2SO_3

TSAg. As was found with cysteine more silver is bound at the end-point with increasing concentration of TSH (Table V). The error is decreased markedly in the presence of 0.1 *M* sulfite and is less than 2% at TSH concentrations smaller than $5 \cdot 10^{-4}$ *M*. Thus the amperometric titration with silver in the presence of sulfite is suitable for the determination of small concentrations of thioglycolic acid and also of its disulfide.

TABLE V

TITRATION OF THIOGLYCOLIC ACID IN 0.25 *M* AMMONIUM NITRATE 0.1 *M* AMMONIA BUFFER

$E_{applied} = -0.3$ V

Molarity of TSH	*$AgNO_3$ used*		*mg TSH*		*Error %*	*Addition*
	ml	*Molarity*	*Taken*	*Found*		
$2 \cdot 10^{-4}$	0.60	$2 \cdot 10^{-2}$	0.9212	1.105	+20	
$4 \cdot 10^{-4}$	1.20	$2 \cdot 10^{-2}$	1.8424	2.211	+20	
10^{-3}	0.665	10^{-1}	4.606	6.12	+33	
$2 \cdot 10^{-3}$	1.34	10^{-1}	9.212	12.345	+34	
$2 \cdot 10^{-4}$	0.51	$2 \cdot 10^{-2}$	0.921	0.939	+2.0	0.1 *M* Na_2SO_3
$5 \cdot 10^{-4}$	1.27	$2 \cdot 10^{-2}$	2.303	2.34	+1.6	0.1 *M* Na_2SO_3
10^{-3}	1.04	$5 \cdot 10^{-2}$	4.606	4.785	+4.0	0.1 *M* Na_2SO_3

2-Mercaptoethanol (ESH)

As may be seen from Table VI solutions with a concentration varying between $5 \cdot 10^{-5}$ and $1.2 \cdot 10^{-3}$ *M* ESH can be titrated with an accuracy and precision within 2.5%. Neither 0.1 *M* sulfite nor 0.1 *M* chloride interfere. The method can be used for the determination of the disulfide ESSE in an ammonia buffer in the presence of 0.1 *M* sulfite:

$$ESSE + SO_3^{-2} \rightleftharpoons ESSO_3^- + ES^-$$

Near the end-point the establishment of this equilibrium was relatively slow when there is some unreacted ESSE left and it was necessary to wait from one to two minutes after addition of silver before a constant current reading was found. With excess of silver a steady current was found immediately after addition of reagent. Solutions which were $1.6 \cdot 10^{-4}$ and $3.2 \cdot 10^{-4}$ *M* in ESSE, 0.1 *M* in Na_2SO_3, 0.2 *M* in NH_4NO_3 and 0.1 *M* in NH_3 were titrated with an error of $\pm 1\%$.

TABLE VI

TITRATION OF ESH IN 0.25 *M* AMMONIUM NITRATE–0.1 *M* AMMONIA BUFFER

$E_{applied} = -0.3$ V

Molarity of ESH	*$AgNO_3$ used*		*mg ESH*		*Error %*	*Addition*
	ml	*Molarity*	*Taken*	*Found*		
$5.07 \cdot 10^{-5}$	0.248	10^{-2}	0.198	0.194	−2.0	
$1.014 \cdot 10^{-4}$	0.495	10^{-2}	0.396	0.387	−2.6	
$1.52 \cdot 10^{-4}$	0.760	10^{-2}	0.594	0.593	−0.2	
$2.028 \cdot 10^{-4}$	1.035	10^{-2}	0.792	0.808	+2.0	
$4.056 \cdot 10^{-4}$	0.832	$2.5 \cdot 10^{-2}$	1.584	1.623	+2.4	
$6.084 \cdot 10^{-4}$	1.230	$2.5 \cdot 10^{-2}$	2.376	2.406	+1.3	
$10.14 \cdot 10^{-4}$	0.520	10^{-1}	3.961	4.06	+2.5	
$5 \cdot 10^{-5}$	0.240	10^{-2}	0.195	0.187	−4.0	0.1 *M* Na_2SO_3
10^{-4}	0.490	10^{-2}	0.391	0.383	−2.0	0.1 *M* Na_2SO_3
$2 \cdot 10^{-4}$	0.995	10^{-2}	0.781	0.777	−0.5	0.1 *M* Na_2SO_3
$4 \cdot 10^{-4}$	0.512	$4 \cdot 10^{-2}$	1.563	1.60	+2.4	0.1 *M* Na_2SO_3
$8 \cdot 10^{-4}$	0.987	$4 \cdot 10^{-2}$	3.126	3.084	−1.3	0.1 *M* Na_2SO_3
$1.2 \cdot 10^{-3}$	1.520	$4 \cdot 10^{-2}$	4.689	4.63	−1.3	0.1 *M* Na_2SO_3
$2 \cdot 10^{-4}$	0.395	$2.5 \cdot 10^{-2}$	0.781	0.790	−1.2	0.1 *M* NaCl
$4 \cdot 10^{-4}$	0.812	$2.5 \cdot 10^{-2}$	1.563	1.585	+1.5	0.1 *M* NaCl
10^{-3}	2.012	$2.5 \cdot 10^{-2}$	3.91	3.933	+0.6	0.1 *M* NaCl

DISCUSSION

Our results with cysteine agree with those of SLUYTERMAN[6] and of BURTON[8]. SLUYTERMAN reports 8% low results with reduced glutathione but in agreement with BURTON AND INGRAM[9] we obtained theoretical results. With thioglycolic acid the positive error is about one half of that found with cysteine. As suggested by SLUYTERMAN both the carboxylate and the amino group in cysteine seem to be responsible for the binding of silver by RSAg, while the smaller error in thioglycolic acid is due to the carboxylate group. The fact that SLUYTERMAN found 8% high results with the ethyl ester of cysteine tends to show that the amino group contributes some to the binding of silver by RSAg. In the absence of silver binding groups (unsubstituted mercaptans, mercaptoethanol) the end-point is found at a molar ratio of sulfhydryl to silver 1 : 1. With the peptide (reduced)glutathione (GSH) and also with serum albumin[15] the end-point is also found at the stoichiometric ratio. However, in acid medium (pH 2

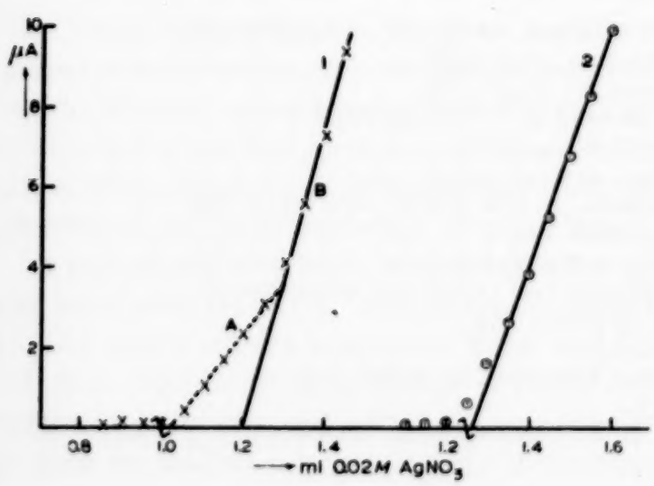

Fig. 2. Titration of thioglycolic acid in buffer 0.25 *M* in ammonium nitrate and 0.1 *M* in ammonia. $E_{applied}$ −0.3 V (1) $4 \cdot 10^{-4}$ *M* TSH; (2) $5 \cdot 10^{-4}$ *M* TSH in presence of 0.1 *M* sulfite. ⌃ indicates equivalence point [TSAg].

to 5.2) GSH and silver react to give insoluble GSAg which reacts with a second equivalent of silver to form a soluble complex.

It is interesting to note that the error obtained with thioglycolic acid is reduced to zero in the presence of 0.1 *M* sulfite, while under these conditions the error of the cysteine titration is reduced to zero only when the RSH concentration is equal to or less than $5 \cdot 10^{-5}$ *M*. The error becomes one half of that observed in the absence of sulfite at concentrations greater than 10^{-5} *M*. It may be of interest to further study the effect of relatively mild complex formers with silver on the titration of thiol compounds with other reactive groups. The striking effect of sulfite on the TSH titration is illustrated in Fig. 2. In the absence of sulfite the first excess of reagent line (A in Fig. 2) is almost straight. In the example in Fig. 2 it intersects with the abscissa at a point corresponding to an error of +2.0%, while reagent line (B) indicates an end-point which is 20% high. The improvement of the situation by 0.1 *M* sulfite is clear from a comparison of titration lines 1 and 2.

ACKNOWLEDGEMENT

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SUMMARY

Results of amperometric argentimetric titrations at the rotated platinum wire electrode in ammonia buffers of cysteine, glutathione, thioglycolic acid and 2-mercaptoethanol are presented. The method gives satisfactory results with glutathione and 2-mercaptoethanol. Thioglycolic acid gives good results in the presence of sulfite but high results in its absence. Its disulfide can be titrated accurately in the presence of sulfite. In agreement with other workers it was found that cysteine yields high results. The error increases with increasing cysteine concentration and is reduced in the presence of 0.1 *M* sulfite. It becomes equal to zero at cysteine concentrations equal to or smaller than $5 \cdot 10^{-5}$ *M*.

RÉSUMÉ

Les auteurs ont effectué une étude du dosage ampérométrique de cystéine, gluthathione, acide thioglycolique et mercaptoéthanol, par titrage argentimétrique.

ZUSAMMENFASSUNG

Beschreibung einer amperometrischen Methode zur Bestimmung von Cystein, Glutathion, Thioglycolsäure und 2-Mercapto-äthanol durch argentometrische Titration.

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PRECISION NULL-POINT POTENTIOMETRY

DIRECT MICRODETERMINATION OF IODIDE IN SOLUTIONS WITH HIGH CHLORIDE CONCENTRATIONS

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Recently precision null-point potentiometric techniques were developed which provided high sensitivity, speed, simplicity and accuracy for the micro determination of chloride in water samples[1], blood serum[2], and solutions obtained by decomposing organic fractions containing chlorinated compounds[3]; and the general principles of the measurement method were presented[4,5]. The same general technique is now described for the direct determination of iodide in the presence of large amounts of chloride, as found in brines or iodized salt. In iodized salt the sodium chloride weight usually exceeds the iodide by a factor of 10,000 to 200,000, and in brines the chloride weight exceeds the iodide by hundreds to thousands of times.

The determination of iodide in brines, iodized salt or similar samples is generally performed by separation of the iodide after oxidation and subsequent measurement by titration[6-8]. The separation is often necessary because the high ratio of chloride to iodide invalidates the measurement method. However, it is shown that a separation of iodide from chloride is not necessary by the precision null-point potentiometric technique. Since the measurement is also rapid it is possible to perform a complete analysis in about 3 min, including weighing the sample, addition of reagents, measurement, and calculation of results.

THE IODIDE MEASUREMENT METHOD

The null-point method is based on rapidly changing the iodide concentration of a prepared unknown sample until it is the same concentration as a constant reference iodide solution, using a potentiometric system to indicate the null-point. The requirements of the method include specific electrodes for iodide, electrical contact between the reference and unknown solutions without significant mixing of the two, and the absence of junction potentials or polarization of electrodes.

A pair of silver–silver iodide electrodes are sensitive to iodide concentration and can be readily prepared. The electrical contact is provided by an asbestos fiber sealed in the small reference-solution tube which is bathed in the beaker of unknown solution. The junction potential is made negligible by preparing the reference and unknown solutions and added reagents to have nearly the same ionic strength. This is done by adding a large amount of electrolyte to all solutions and by diluting the

brines or salt samples 100 to 1. Therefore, the electrolyte contribution by the sample is quite small in comparison with the contribution by the reagents. A high input-impedance measuring system prevents polarization of electrodes.

For speed of analysis it is desirable to have continuous indication on the null meter and continuous mixing and addition of reagent until the solutions are of equal concentration. An efficient stirring and measurement system and an arrangement so both solutions reach the same temperature rapidly have been described[1,2].

APPARATUS

Although the general type of equipment for the precision null-point potentiometric determination of iodide was the same for iodide as previously used for chloride determinations[1,2], there were the following specific differences:

Electrodes

The Ag–AgI electrodes were prepared by iodizing a pair of silver-plated platinum electrodes sealed in glass. The platinum electrodes were made by connecting approximately 3 × 10 mm platinum plates to platinum wires by flash welding and sealing the top edge of the platinum plate into 4-mm O.D. soft glass tubing. After thoroughly cleaning the platinum plates in boiling nitric acid and washing in demineralized or distilled water, the electrode pair was plated for 3 h at 2 mA/cm^2 in a solution of $KAg(CN)_2$ (about 10 g $KAg(CN)_2$/l) which was stirred during the plating process. The electrodes were then washed for 4 h in running tap water and finally for 2 h in running demineralized water.

The electrodes were iodized in an iodide solution (1 drop of concentrated HI per 100 ml of 0.05 *M* KI solution) for 12 min at 2 mA/cm^2. Inmediately after preparation the electrodes were washed in demineralized water for about 5 min, placed in a beaker containing reference solution, and kept in the dark until used.

Because the Ag–AgI electrodes are sensitive to light, it is best to prevent exposure of the electrodes to continuous room light, either during use or storage. In the present work, the room lights were turned off at night or the window shades pulled during the day so that the only light striking the electrodes came through adjoining doors to the room and from around the window shades. A closed titration compartment such as available with the Sargent Spectro-Electro titrator[9] eliminates the need for a room with subdued light.

Mixing in reference compartment

In order to be more certain of good stability during the null-point measurements it was found advantageous to vibrate the electrode continuously in the reference compartment by means of attaching the electrode to an alligator clip mounted so that a piece of spring steel, also attached to the clip, pressed firmly against the top knurled nut of the stirrer chuck on the electrode stand[9]. As the stirrer turned it caused a small vibration of the reference electrode which improved the stability of the measured voltage.

Null detector

A high input impedance Sargent comparator (E. H. Sargent Co., Chicago 30, Ill.) was used as the null detector.

REAGENTS

The null, sample, and concentration variation solutions are all prepared to contain 40,000 p.p.m. sodium acetate and 25,000 p.p.m. acetic acid. These readily available reagents usually contain negligible iodide and also buffer the solutions to provide stability of the iodide. Sodium chloride is also added to the reagent solutions when analyzing brines and iodized salt. The sodium chloride concentration is nearly the same in all samples of iodized salt so the reagents can be prepared to have the same concentration as the samples. However, the chloride concentration in brines may vary over a large range so the reagents are prepared to have a concentration of sodium chloride which is intermediate in the usual range. Although the range of chloride is large and other salts are present the over-all differences in ionic strength of sample and reagents is not large when solutions are properly prepared.

Stock solutions

KI solution. Several l of 10 mg I^-/l were prepared by weighing out reagent grade potassium iodide and diluting to volume with deionized water.

NaCl solution. 1.000 l of 1.000 *N* NaOH was added to 1.000 l of 1.000 *N* HCl. Sodium chloride was prepared in this manner rather than using reagent grade sodium chloride because of the relatively large concentration (about 0.002%) of impurity iodide in the salts available.

Electrolyte solution. Each l contained 80.0 g reagent grade sodium acetate and 50.0 ml reagent grade acetic acid diluted to volume with deionized water. If several hundred samples are to be run it is best to prepare 10 l or more of this reagent.

Standard solutions for brine-type samples

Null reference solution A (1.000 mg I^-/l). For each l, 500 ml of stock electrolyte, 10 ml stock NaCl, and 100.0 ml of stock KI solutions were mixed and diluted to volume with deionized water.

Standard dilution reagent B. It is prepared the same as the null reference solution A except with no stock KI added.

Standard addition reagent C. It is prepared the same as reagent A except that 200.0 ml of stock KI are added for each l.

Standard solutions for iodized salt

Null reference solution D (0.500 mg I^-/l). For each l 500 ml of stock electrolyte, 200 ml stock NaCl, and 50.0 ml of stock KI solutions were mixed and diluted to volume with deionized water.

Standard dilution reagent E. It is prepared the same as reagent D except that no stock KI is added.

Standard addition reagent F. It is prepared the same as reagent D except that 100.0 ml of stock KI is added per l.

PROCEDURES

Preparation of samples for analysis

If brine samples have 10–200 p.p.m. iodide or iodized salt samples have 5–100 p.p.m. iodide, weigh 1.000 g and transfer into a 100-ml volumetric flask, add 50.0 ml of stock

electrolyte solution, dilute to volume with deionized water, and mix. If brine or salt has more or less iodide than in the given ranges, a smaller or larger sample could be taken and the same procedures used.

Establishment of the null point

At the beginning of each day the isolation compartment is emptied and filled to at least a few ml above the top of the Ag–AgI electrode with null reference solution A or D, depending on sample type. The method of establishing the nullpoint is the same as for chloride determinations.

Measurement of iodide concentration

After setting the nullpoint, the reference solution in the beaker is removed, and a beaker containing 20.00 ml of prepared sample is placed into position, the stirrer started and, depending on the direction of deflection of the null meter, either addition or dilution reagent is added from the appropriate buret (at a delivery rate of about 15 ml/min or less) until the nullpoint is nearly reached, at which time delivery of reagent is stopped. Small increments of reagent are then added by rapid rotation of the stopcock until the nullpoint is reached, the buret reading recorded to obtain V_a, and the iodide concentration calculated using equation (2) for brines and equation (3) for iodized salt.

CALCULATIONS

The concentration of iodide in p.p.m. is expressed by the general equation (1).

$$\text{p.p.m. iodide} = \frac{C_R}{W_s}(V_o \pm V_a) \qquad (1)$$

where W_s is the weight in g of the sample actually measured, C_R is the iodide concentration of the null reference solution in mg/l or μg/ml, V_o is the volume in ml of prepared solution taken for measurement (20.00 ml in the given procedure) and V_a is the volume of standard addition or dilution reagent added in reaching the nullpoint. If addition reagent is delivered, then V_a is subtracted from V_o, and if dilution reagent is delivered V_a is added to V_o.

Equation (1) reduces to equation (2) for brines using a 1.000-g original sample (0.2000 g measured sample), null solution A, and reagent B or C.

$$\text{p.p.m. iodide} = 5\,(20.00 \pm V_a) \qquad (2)$$

Equation (1) reduces to equation (3) for iodized salt using a 1.000-g original sample, null solution D, and reagent E or F.

$$\text{p.p.m. iodide} = 2.5\,(20.00 \pm V_a) \qquad (3)$$

RESULTS

The results presented in Table I illustrate the precision and accuracy for iodide determination in samples containing a wide range of chloride, typical of brine samples. Two samples contain 10,000 p.p.m. each of calcium chloride, magnesium chloride, and sodium sulfate in addition to the sodium chloride. The sodium chloride concentration

TABLE I

DETERMINATION OF IODIDE IN 0.2000 g OF BRINE-TYPE SAMPLES BY PRECISION NULL-POINT POTENTIOMETRIC METHOD

Quantity of iodide[a], *μg*	*Concentration of iodide in sample, p.p.m.*		*Weight ratio of chloride to iodide*
	known	*found*[b]	
40.12	200.0	200.6 ± 0.6	0
40.00	200.0	200.0 ± 0.3	175
39.80	200.0	199.0 ± 0.5	300[c]
40.00	200.0	200.0 ± 0.6	350
39.76	200.0	198.8 ± 0.3	500
10.00	50.0	50.0 ± 0.2	0
9.96	50.0	49.8 ± 0.2	1000[c]
10.12	50.0	50.6 ± 0.3	1400
3.94	20.0	19.7 ± 0.3	1800
1.90	10.0	9.5 ± 0.3	3500

[a] Average amount of iodide actually measured in 5 20-ml aliquots of prepared solutions containing 0.2000 g of sample.
[b] Reproducibility is given as standard deviation for 5 samples.
[c] Samples contained about 10,000 p.p.m. each of $CaCl_2$, $MgCl_2$ and Na_2SO_4 as well as the large amount of NaCl.

TABLE II

DETERMINATION OF IODIDE IN 0.2000 g OF IODIZED SALT BY PRECISION NULL-POINT POTENTIOMETRY

Quantity of iodide measured, μg	*Concentration of iodide in samples, p.p.m.*	
	known	*found*[a]
20.00	100.0	100.0 ± 0.4
6.16	30.0	30.8 ± 0.4
3.98	20.0	19.9 ± 0.2
1.92	10.0	9.6 ± 0.3
1.28	6.7	6.4 ± 0.1
0.88	5.0	4.4 ± 0.2

[a] Reproducibility is given as standard deviation for 5 measured samples.

varies from 10,000–200,000 p.p.m. in the original sample, before the 100 to 1 dilution for measurement of iodide.

The samples presented in Table II have a larger chloride to iodide ratio as would occur in iodized salt samples. With these samples there is some lag in the response of the electrodes, but reagent can still be added at about 15 ml/min. If the null point should accidently be overshot, it can be approached from the opposite side by delivering appropriate reagent and subtracting this volume from that previously added. It is necessary to check the nullpoint after every 2–3 determinations because of a small drifting of the electrodes.

SUMMARY

The determination of micro amounts of iodide in the presence of large concentrations of chloride, such as found in brines or iodized salt, can be performed directly and rapidly by the precision

null-point potentiometric method. The complete analysis time is about 3 min. Iodized salt samples containing 5–100 p.p.m. iodide were determined with an average deviation less than 0.3 p.p.m. and with relative errors of about 0.5% at 100 p.p.m. and about 5% at 10 p.p.m. iodide. The measured samples contained 1–20 μg of iodide in 20 ml of solution, and the sodium chloride to iodide weight ratio was as high as 200,000 to 1. Similar precision and accuracy were obtained for prepared brines containing 10–200 p.p.m. iodide and a wide range of chloride to iodide ratios.

RÉSUMÉ

Une méthode potentiométrique est proposée pour le microdosage des iodures, en présence de fortes concentrations en chlorures. Ce procédé est précis et très rapide.

ZUSAMMENFASSUNG

Beschreibung einer potentiometrischen Bestimmung von sehr kleinen Mengen Jod in Gegenwart von grossen Mengen Chlorid.

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Short Communication

Colorimetrische Bestimmung von Strontium

Zur colorimetrischen Bestimmung von Strontium schlugen LUCCHESI *et al.*[1] die Chloranilsäure (2,5-Dichloro-3,6-dihydrochinon) vor. Diese Methode hat einige Nachteile; z.B. ist es notwendig, das Reaktionsgemisch 3 Stunden bei 0° stehen zu lassen, damit die Reaktion quantitativ verläuft.

Andere Reagentien zur colorimetrischen Bestimmung von Strontium sind noch nicht vorgeschlagen worden. Auch die Möglichkeit der Verwendung der Dilitursäure (5-Nitrobarbitursäure, 5-Nitro-2,4,6-trioxohexahydropyrimidin), die mit Strontium bereits bei Zimmertemperatur ein unlösliches Diliturat liefert (Löslichkeit[2] in Wasser bei 25°: 1.7 Mmol/1000 ml) wurde bis jetzt noch nicht untersucht. Anwendungen der Dilitursäure sind nur bekannt für die gravimetrische[3], volumetrische[4] und colorimetrische[5,6] Bestimmung von Kalium und Magnesium[8].

Die Herstellung der Dilitursäure erfolgte durch Nitrieren von Barbitursäure[7]. Das zweimal umkristallisierte Produkt wurde durch den Schmelzpunkt identifiziert. Für die Versuche wurde eine 0.05 *N* Lösung von Dilitursäure verwendet; zur Verminderung des infolge der geringen Löslichkeit von Strontiumdiliturat entstehenden Fehlers wurde die Lösung mit Strontiumdiliturat gesättigt. Die Titerstellung erfolgte durch Titration mit 0.1 *N* Natronlauge und Phenolphtalein als Indikator.

Die Konzentration des Strontiums betrug 0.0 bis 2.0 mg Sr/ml. Die Mischung der

Probe mit dem Reagens (1 : 1) wurde nach 15 min filtriert und die Extinktion des Filtrates bei der Wellenlänge 420 mμ[6] gemessen. Die photometrischen Messungen wurden mit einem Zeiss-Universalspektrophotometer (Cäsium–Antimon-Photozelle MSVB mit Messungsbereich 200–650 mμ, 2-ml Küvetten mit Schichtdicke 0.498 cm) durchgeführt.

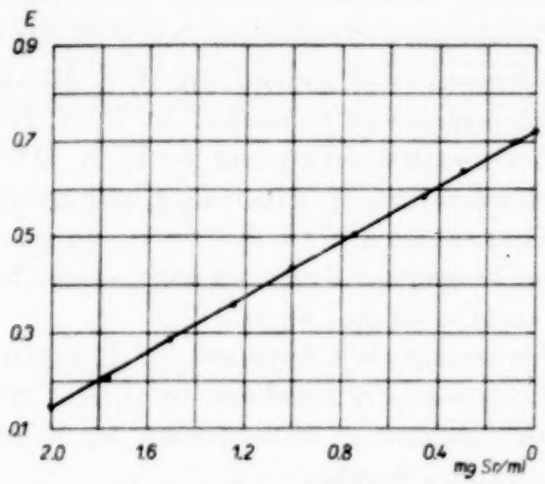

Fig. 1. Kalibrationskurve.

Der beobachtete Maximalfehler betrug + 0.02 mg Sr/ml (relativer Fehler 2.5%); der durchschnittliche Fehler bei 2 Messungen derselben Probe betrug ±0.006 mg Sr/ml.

In Übereinstimmung mit früher gemachten Beobachtungen bei colorimetrischen Bestimmungen mit Dilitursäure wurden die folgenden Ionen als störend festgestellt: NH_4, K, Sn, Fe(II), Fe(III), Cr, Cd, Cu, Mn, Ca, Ba, Zn, Co, Ni, Hg(I), Ag und Pb; ferner die farbigen Anionen CrO_4^{-2}, $Cr_2O_7^{-2}$, MnO_4^- und $Fe(CN)_6^{-4}$. Ohne Einfluss sind: NO_3^-, SO_4^{-2}, SO_3^{-2}, PO_4^{-3}, Cl^-, Br^- und I^-.

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NAS-NS 3007, *The Radiochemistry of Chromium*, by J. PIJCK, 30 pp., $0.50.
NAS-NS 3008, *The Radiochemistry of Rhodium*, by G. R. CHOPPIN, 30 pp., $0.50.
NAS-NS 3009, *The Radiochemistry of Molybdenum*, by E. M. SCADDEN AND N. E. BALLOU, 33 pp., $0.50.
NAS-NS 3010, *The Radiochemistry of Barium, Calcium and Strontium*, by D. N. SUNDERMAN AND C. W. TOWNLEY, 115 pp., $1.25.
NAS-NS 3011, *The Radiochemistry of Zirconium and Hafnium*, by ELLIS P. STEINBERG, 48 pp., $0.50.
NAS-NS 3014, *The Radiochemistry of Indium*, by D. N. SUNDERMAN AND C. W. TOWNLEY, 42 pp., $0.50.

Available from the Office of Technical Services, Department of Commerce, Washington 25, D.C.

The Subcommittee on Radiochemistry of the Committee on Nuclear Science, National Academy of Sciences, National Research Council, with the aid of the U.S. Atomic Energy Commission is undertaking a laudable program of bringing out authoritative monographs on the radiochemistry of the various elements. Recognizing the need for an up-to-data compilation of radiochemical information and particularly laboratory procedures, the committee plans a series of monographs, each written by an expert on the element in question and designed to be of maximum usefulness to the worker at the laboratory bench.

A more or less standard format is followed, deviations occurring where it would otherwise be inappropriate to the element in question, and the sequence in the monograph on cadmium may be taken as typical. First, there is a section giving a general review of the inorganic and analytical chemistry of the element. This is followed by a survey of its radiochemical behavior and a table of isotopes. Next is a brief summary of the chemical properties having particular interest for radiochemists, including such characteristics as oxidation states, complexes, insoluble compounds, and extractability. A section is usually devoted to dissolution of samples and another to counting techniques. Finally, there is a collection of radiochemical procedures given in detail for direct laboratory application.

As in any such undertaking, the quality of the effort varies with the individual

author. One could wish that some of the authors had prepared their material with more attention to detail: there are minor annoyances such as author's names misspelled in literature references, misprints, and the inclusion in the tables of equilibrium constants of some numerical values which do not stand up under critical examination. Much more care appears to have been devoted to the radiochemical procedures, and it is in these that the real value of the series will lie. The monographs can be recommended as useful for the purpose for which they were written and should be of interest not only to radiochemists but also to workers in geochemistry, activation analysis, biochemistry, nuclear engineering, and other fields in which there is occasion to use radiochemical techniques.

Massachusetts, Institute of Technology DAVID N. HUME

Anal. Chim. Acta, 24 (1961) 98–99

Radiometric Trace Analysis of Lead par P. C. VAN ERKELENS, Drukkerij Smits, Oudegracht 231, Utrecht, 1960, 104 pp.

À l'encontre de ce que laisse supposer le titre, ce livre n'a pas pour objet une étude bibliographique complète du dosage radiométrique du plomb. L'auteur a recours aux études déjà effectuées dans ce domaine mais il expose surtout ses propres travaux, les essais préliminaires comme les résultats positifs et négatifs qu'il a obtenus.

En fait, toutes les méthodes radiochimiques n'ont pas été mises à l'épreuve ainsi que l'indique le titre de l'ouvrage; il n'est pas question, par exemple, des méthodes par activation aux neutrons, qui ne présentent sans doute pas assez de sensibilité pour les applications que l'auteur veut en faire.

Les méthodes utilisant un réactif radioactif (R.R.) et celle qui est basée sur les échanges (R.E.) ont par contre été très minutieusement examinées. La lecture de cet ouvrage sera très profitable à tous et plus spécialement à ceux, trop nombreux encore, qui utilisent les méthodes de dosage de traces avec une rare désinvolture: le choix des réactifs, la détermination, la pureté de ceux-ci, les pertes et contaminations, le comportement des ions étrangers, l'étude minutieuse des diverses opérations analytiques, tous ces problèmes font l'objet d'examens approfondis et montrent que de tels dosages ne s'improvisant pas.

L'auteur arrive aux conclusions suivantes: deux méthodes se prêtent particulièrement bien à ce dosage: l'analyse R.R. avec le phosphate marqué au phosphore 32, qui permet de doser 1 μg de plomb; elle est relativement simple, mais plusieurs ions étrangers gênent, une liste en est donnée avec les quantités limites. L'analyse R.E. mise au point par l'auteur basée sur une extraction doublée d'un échange entre le plomb et le thallium et une mesure finale de l'activité du Tl 204. La déviation standard est de 11% pour 0.1 μg de plomb.

Ouvrage remarquable par la précision des techniques décrites.

D. MONNIER (Genève)

Anal. Chim. Acta, 24 (1961) 99

Gas Chromatography Abstracts 1959, edited by C. E. H. KNAPMAN, Assistant editor: C. G. SCOTT, Butterworths, London, 1960, Prix 42s.

Ce volume d'abstracts est la suite de celui publié l'année dernière (Gas Chromatography Abstracts, 1958) et recensé dans cette revue.

Le „Gas Chromatography Discussion Group" a estimé qu'il était nécessaire de poursuivre l'effort commencé, d'autant plus que le nombre de travaux effectués dans ce domaine ne cesse de croître et qu'il est impossible même aux spécialistes de se tenir au courant de tous les articles qui paraissent. Les auteurs ont répertorié 717 articles. De chacun d'eux, ils donnent le titre, le nom du ou des auteurs, celui du périodique avec la page, le numéro et l'année, puis un bref compte rendu de 3 à 6 lignes.

En fin d'ouvrage, une table alphabétique des auteurs et une table des sujets permettent de retrouver facilement l'article recherché.

D. MONNIER (Genève)

Anal. Chim. Acta, 24 (1961) 100

Physical Methods in Chemical Analysis, Edited by WALTER G. BERL, Vol. I, 2nd revised edition, xiv + 686 pp., Academic Press, New York and London, 1960, Prix 19$.

La première édition du premier volume de cet ouvrage est de 1950, elle a été présentée par N. STRAFFORD dans cette revue (*Anal. Chim. Acta*, 5 (1951) 334).

Les têtes de chapitres n'ont pas été modifiées; quelques collaborateurs ont été adjoints ou changés. C'est ainsi que l'exposé sur la diffraction des rayons X appliquée aux fibres est l'oeuvre de J. A. HOWSOM ET N.M. WALTER, que le chapitre traitant de la spectrophotométrie est présenté par W. R. BRODE ET M. E. CORNING, que la microscopie électronique a été confiée à R. D. HEIDENREICH ET C. J. CALBRICK et la spectrométrie de masse à C. F. ROBINSON. Quant à la polarométrie, elle ne fait plus partie de ce volume.

La bibliographie a été complétée, elle va jusqu'en 1959. Elle n'est pas très étendue car les auteurs n'ont retenu que les articles et les livres les plus importants.

Chaque méthode est présentée avec soin, les principes fondamentaux en sont exposés de façon claire et logique. Les auteurs auraient peut-être pu s'étendre davantage sur les problèmes purement analytiques tels que: possibilités des divers processus, sensibilité, précision, applications au dosage des traces. Tel qu'il est, ce traité a déjà rendu et rendra encore de signalés services à tous ceux qui ont recours aux méthodes physicochimiques d'analyse.

D. MONNIER (Genève)

Anal. Chim. Acta, 24 (1961) 100

THE EFFECT OF VARIATIONS IN BAROMETRIC PRESSURE AND OTHER FACTORS ON THE EBULLIOSCOPIC DETERMINATION OF MOLECULAR WEIGHTS, WITH SPECIAL REFERENCE TO THE USE OF THE MENZIES DIFFERENTIAL THERMOMETER

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INTRODUCTION

The ebullioscopic determination of the molecular weight of a substance, *i.e.* that involving the measurement of the elevation of the boiling point of a solvent by the substance, is a well established classical procedure; however, when results correct to ± 1–2% or better are required, several effects which are usually ignored may become significant, especially when the boiling point elevation is measured with a MENZIES differential thermometer[1]. Four such effects are considered below, *viz.*

(*1*) the effect of reading only the level in the capillary limb of the MENZIES differential thermometer,

(*2*) the effect of the ebullioscopic elevation on the sensitivity of the MENZIES differential thermometer,

(*3*) the effect of variations in barometric pressure on the ebullioscopic constant of the solvent, and

(*4*) the effect of variations in barometric pressure on the sensitivity of the MENZIES differential thermometer.

These effects are considered with special reference to the semi-micro and micro ebullioscopic methods of COLSON[2], since these possess several advantages (notably in the amount of sample required) over earlier methods; moreover, the semi-micro method has been extended in scope to cover a wider range of solvents and to include the use of a differential thermometer filled with benzene (instead of water) to obtain greater sensitivity when using low boiling solvents[3]. It is shown that while effects (*1*) and (*2*) are not significant in COLSON's methods, effects (*3*) and (*4*) are, *i.e.* although the small variations in barometric pressure normally encountered *during a single ebullioscopic experiment* using a MENZIES differential thermometer have no significant effect, the larger variations in barometric pressure *between different experiments* may be significant. Expressions are therefore developed to account for the effect of variations in barometric pressure, and correction terms allowing for this are calculated for use with some common solvent–thermometer combinations[3].

THE MENZIES DIFFERENTIAL THERMOMETER

Since three of the four effects considered [(*1*), (*2*) and (*4*)] apply only when the MEN-

ZIES differential thermometer is used, the main features of this thermometer are summarised.

The MENZIES differential thermometer in its usual form[1-5] is a U-tube manometer in which one limb is simply a bulb (the lower bulb); this connects by capillary tubing (the capillary limb) to another bulb (the upper bulb). The thermometer is approximately half-filled with a liquid (usually water) and is sealed after evacuation so as to exclude air; it therefore contains only the filling liquid and its vapour. Differences in temperature between the lower and upper bulbs cause differences in vapour pressure in the bulbs, which in turn lead to differences in level between the liquid in the lower bulb and that in the capillary limb. In ebullioscopy the thermometer is positioned in the ebulliometer so that the lower bulb is subjected to the efflux of boiling solution from the Cottrell pump whereas the upper bulb is surrounded by solvent vapour. Initially, with a pure solvent boiling without super-heating, both bulbs are ideally at the same temperature and the difference in level between the liquid in the lower bulb and that in the capillary limb is simply the capillary rise due to surface tension; in practice the difference is usually increased slightly by unavoidable super-heating of the solvent and by the elevation of boiling point due to any residual impurities. On the addition of non-volatile solute the resulting elevation of boiling point causes the lower bulb to increase in temperature, whereas the upper bulb remains at the same temperature, *i.e.* at the boiling point of the solvent; this results in a rise of the liquid level in the capillary limb and a corresponding fall in the level in the lower bulb; the difference in height between the two levels can be measured if the thermometer has a scale engraved on it or if the levels are observed through a cathetometer. An important feature is that, unlike those ebulliometers where the elevation of boiling point is read on a single Beckmann thermometer surrounded by boiling solution, the small barometric fluctuations normally encountered *during the experiment* do not cause significant error, since both bulbs are affected equally. Moreover, at the temperatures encountered in ebullioscopy, the differential thermometer is more sensitive than the ordinary type of Beckmann thermometer, *e.g.* a 1-mm rise on a Beckmann thermometer represents a rise of approximately 0.02°, but on a water-filled differential thermometer it represents about 0.005° at 80° and 0.002° at 110°. The other advantages of the differential thermometer over the Beckmann type are enumerated by MENZIES[1].

As shown by the preceding figures, the sensitivity of the differential thermometer, unlike the conventional mercury thermometer, increases markedly with temperature. It depends on the density-temperature and the vapour pressure-temperature relationships of the filling liquid; this is usually water, in which case temperature differences can be converted from mm head of water to ° by multiplying by the factor given by MENZIES in his conversion table[1] for temperatures up to 102°, and by interpolating from the values calculated by KITSON AND MITCHELL[5] for temperatures above 102°.

In certain instances it may be desirable to employ a filling liquid other than water in order to obtain greater sensitivity when using a low boiling solvent (*e.g.* benzene-filled thermometer with acetone as solvent[3,5]). Although conversion tables for non-aqueous filling liquids do not appear in the literature, they may be constructed if the density–temperature and the vapour pressure–temperature relationships of the filling liquid are known[5] (but see the footnote to equation 4.5 below).

PRELIMINARY CONSIDERATION OF THE MAGNITUDE OF THE EFFECTS

(*a*) *Effect of reading only the level in the capillary limb of the Menzies differential thermometer*

The table of factors given by MENZIES[1] converts to °C the head of water measured in mm, *i.e.* the difference in levels between the menisci in the lower bulb and in the capillary limb. It is general practice, however, to observe only the level in the capillary limb; it is obvious that if this level rises the level in the lower bulb must fall by an amount depending on the ratio of the cross-sectional areas of the lower bulb and the capillary limb (the thermal expansion of the filling liquid can be ignored for the small temperature differences encountered). For example, the thermometer used in COLSON's semi-micro method[2] has a lower bulb approx. 7 mm in diameter and a 1-mm capillary, giving a cross-sectional ratio of approx. 50 : 1. A rise in the level of 1 mm in the capillary limb is therefore accompanied by a fall of approx. 0.02 mm in the level in the lower bulb and thus represents a total change of level of 1.02 mm. Although those operators who convert from mm head of water to °C usually observe only the level in the capillary limb, they obtain the total change of level by referring to a previously constructed graph relating the two values[4,6]; this is considered to be both more convenient and more reliable than reading both levels. An alternative procedure for those thermometers which carry etched scales would be (by analogy with the Kew pattern barometer) to contract the scale on the capillary limb by an appropriate factor depending on the ratio of the cross-sectional areas of the lower bulb and capillary limb, *e.g.* by 0.98 in the above numerical example; the reading on the capillary limb would then represent directly the total change in level. However, this does not seem to have been attempted in the literature.

For COLSON's semi-micro method[2] and its extended modification[3], in which a compound of known molecular weight is used as a standard and in which it is therefore unnecessary to convert the differential thermometer reading to °C, it seems preferable to adhere to his practice of observing only the rise in level in the capillary limb and recording this as the temperature elevation in mm. (Although COLSON converts the rise in level in the capillary limb directly to °C in his micro method[2], the constant error introduced cancels out when the molecular weight of the sample is compared with that of the standard compound). The practice of recording the temperature elevation in mm is in any case obligatory when using a thermometer filled with a non-aqueous liquid since there are then no published conversion tables.

The above arguments have a bearing on thermometer design and filling, in that it seems advisable not to make the lower bulb too narrow in diameter, so as to minimise the effect of any slight inconsistencies in bore, and neither to overfill nor underfill, so that the liquid meniscus never traverses the two ends of the bulb where the diameter necessarily becomes narrower.

(*b*) *The effect of the ebullioscopic elevation on the sensitivity of the Menzies differential thermometer*

One effect arising from the temperature dependence of the sensitivity of the MENZIES differential thermometer is due to the fact that as the temperature of the lower bulb (in contact with the boiling solution) necessarily increases during the course of an ebullioscopic molecular weight determination, the sensitivity of the thermometer

correspondingly increases. Whether the increase is significant depends upon the magnitude of the temperature elevations encountered, which in turn depends upon the solute concentrations employed. When, as is generally the case in the literature, solute concentrations of 0.1 molal and over are used, corresponding to temperature elevations of 0.1–0.5° and over (depending upon the solvent employed), then the effect may become significant, *e.g.* taking benzene as ebullioscopic solvent with a water-filled thermometer, and assuming an elevation of 0.5°, then the temperature of the lower bulb is initially say 80.1° and finally 80.6°; the corresponding sensitivities, 4.952 and $4.910 \cdot 10^{-3}$ °C/mm (the latter being the factor for the mean temperature of the upper and lower bulbs, *viz.* 80.35°) differ by 0.9%. The methods by which the effect is allowed for vary: thus MENZIES AND WRIGHT[6] convert each reading of the differential thermometer from mm to °C by applying the appropriate factor corresponding to the mean temperature of the lower and upper bulbs, this temperature being higher than the initial boiling temperature (determined with an ordinary mercury thermometer) by half the observed temperature elevation. On the other hand, BARR AND ANHORN[4] calculate factors which allow simultaneously for both this effect and that described below (d) due to variations in barometric pressure on the sensitivity of the differential thermometer; however, their calculations (for which no details are given) refer only to the use of benzene as solvent with a water-filled differential thermometer in a limited pressure range (720–750 mm), and, moreover, they overcorrect for the effect of the ebullioscopic elevation by applying the MENZIES factor corresponding to the temperature of the lower bulb instead of the mean temperature of the upper and lower bulbs; they also ignore the effect described below *(c)* due to variations in barometric pressure on the ebullioscopic constant.

In COLSON's methods[2] the solute concentrations used are much lower than those described above (rarely exceeding 0.02 molal) and the total elevation rarely exceeds 0.1°. The difference in the factors in the example given above, *viz.* benzene as ebullioscopic solvent with water-filled thermometer, correspondingly rarely exceeds 0.2%, and can therefore be neglected, as indeed it can in all the combinations of ebullioscopic solvent and thermometer filling liquid employed in the extended modification of the semi-micro method[3].

(c) The effect of variations in barometric pressure on the ebullioscopic constant

Since an increase in barometric pressure increases the boiling point T of a solvent or solution, with a consequent decrease in the latent heat of vaporisation c_v, there will be an increase in the ebullioscopic constant K, from the fundamental relationship

$$K = RT^2/1000\, c_v \qquad (3.1)$$

where R is the gas constant; if R is in cal·mole^{-1}·deg.$^{-1}$, T in °K and c_v in cal·g^{-1}, then K will be in deg.·mole^{-1}·kg, *i.e.* deg. per mole of solute for 1000 g solvent. Similarly a decrease in barometric pressure will cause a decrease in the ebullioscopic constant. This increase (or decrease) can be calculated approximately in the following manner: Let the barometric pressure P increase by 10 mm from 760 to 770 mm Hg. Then the increase in boiling point ΔT will be, from Craft's rule[7],

$$\Delta T = CT \cdot 10 \qquad (3.2)$$

where T is the boiling point in °K, and C is 0.00012 for most solvents and 0.00010 for water and alcohols. If now c_v is assumed to be independent of T, (3.1) transforms to

$$K \propto T^2 \tag{3.3}$$

and the ratio of the ebullioscopic constants at 770 and 760 mm Hg will be given by

$$K_{770\text{ mm}}/K_{760\text{ mm}} = [(T + \Delta T)/T]^2, \tag{3.4}$$

$$\simeq 1 + 2\,\Delta T/T, \text{ as } \Delta T \text{ is small compared with } T \tag{3.4a}$$

$$\simeq 1 + 2OC$$

$$\simeq 1.0024 \text{ for most solvents and } 1.0020 \text{ for water and alcohols.}$$

Hence K will increase by approximately 0.20–0.24% per 10 mm increase in pressure. Since c_v, which has been assumed independent of T, actually decreases with increase in T, the above estimate will be slightly low. The value generally quoted in the literature is approximately 0.3% per 10 mm[6], and the more rigorous treatment given below yields values ranging from 0.21% (for ethanol) to 0.29% (for benzene) for eight solvents (Table I).

This effect is generally ignored in the literature, usually justifiably, since it is in general insignificant compared with the other deviations encountered in ebullioscopy, or it is sometimes inadvertently allowed for to some extent by determining the ebullioscopic constant (or a related apparatus constant) using a standard substance of known molecular weight under barometric conditions not differing markedly from those prevailing when the actual molecular weights of samples are being determined.

(d) The effect of variations in barometric pressure on the sensitivity of the Menzies differential thermometer

The effect of variations in barometric pressure on the ebullioscopic constant treated in (c) is perfectly general and independent of the temperature-measuring device employed. However, when using a MENZIES differential thermometer there is a further effect, *viz.* that the variations in barometric pressure, in affecting the boiling point of the solvent or solution, affect the sensitivity of the thermometer. The magnitude of this effect will depend both on the temperature at which the differential thermometer is used and on the liquid with which it is filled; the appropriate expressions are derived below. However, it is instructive to ascertain the magnitude of the effect by calculating it for a typical set of circumstances, *e.g.* using benzene as ebullioscopic solvent with a water-filled thermometer. If, as before, it is assumed that the barometric pressure increases from 760 to 770 mm, then the boiling point of the benzene will increase by approximately 0.43° from 80.10 to 80.53° (*cf.* the value of dt/dp given in Table II below). The table of factors for the water-filled thermometer calculated by MENZIES[1] gives values of 4.952 and $4.879 \cdot 10^{-3}$ °C/mm respectively at these two temperatures. Denoting the ebullioscopic constant, expressed in the units mm rise on the water-filled thermometer per mole of solute for 1000 g solvent, as K',

$$K' \text{ (in mm/mole for 1000 g)} = K \text{ (in °C/mole for 1000 g)}/f \text{ (in °C/mm)} \tag{3.5}$$

Hence

$$K'_{770\text{ mm}}/K'_{760\text{ mm}} = f_{760\text{ mm}}/f_{770\text{ mm}} = 4.952/4.879 = 1.015$$

The above treatment ignores the effect of the increase in barometric pressure on K itself: however, this has been previously shown to be approx. 0.3% per 10 mm increase in pressure, so that the total effect of the 10 mm increase in pressure causes an increase of 1.8% in the ebullioscopic constant K' measured in mm/mole for 1000 g, the major part of the increase (1.5%) being due to the effect of the barometric pressure on the sensitivity of the differential thermometer. The latter effect is clearly significant and cannot be ignored.

(e) Application of the above considerations to the ebullioscopic determination of molecular weights

The foregoing discussion shows that when using temperature measuring devices other than the MENZIES differential thermometer, provided these are used differentially, the only effect which can have possible significance on the results is the variation of ebullioscopic constant with barometric pressure; this is best allowed for by correcting the ebullioscopic constant (or related apparatus constant) to standard atmospheric pressure using the correction terms c_1 given in Table I for the seven solvents listed, or, for other solvents, calculating the term as shown below.

On the other hand, when using a MENZIES differential thermometer all 4 effects may be significant, although under the conditions used by COLSON[2] it has been shown that only the 2 effects due to barometric pressure described in (c) and (d) are significant, particularly the latter. However, COLSON ignores both these effects in his semi-micro method[2] and the former effect in his micro method; in the micro method the latter effect is allowed for by determining the boiling point to 0.1° with a mercury thermometer and, since a water-filled thermometer is used exclusively, by applying the appropriate factor[1]. One way of allowing for all the above effects is to adopt a "bracketing" procedure such as that proposed by SWIETOSLAWSKI[8] and adopted by KITSON *et al.*[9], *viz.* to add alternately the standard reference compound and the sample in the same run, but this makes subsequent recovery of the sample difficult and assumes no interaction in solution; these objections do not apply to COLSON's methods, since the molecular weight of the sample is compared with that of the standard compound in separate runs.

To maintain the advantages of COLSON's methods, while at the same time obtaining consistent results in routine use, *i.e.* over periods when the barometric pressure may be expected to fluctuate over a wide range (*e.g.* 720–780 mm, as in the British Isles), it appears that the simplest procedure would be to apply a single correction, allowing for both pressure effects, which will convert the results obtained at the prevailing barometric pressure to standard atmospheric pressure; this solution is in any case obligatory when using a thermometer filled with a non-aqueous solvent (*e.g.* the benzene thermometer used in the extended semi-micro method[3]), since no tables exist for converting mm to °C in such cases and their compilation would be laborious. The derivation of the appropriate correction terms is accordingly given below, followed by their combination into a single comprehensive term.

DERIVATION OF THE CORRECTION TERMS

(a) The correction term for the effect of variations in barometric pressure on the ebullioscopic constant K

The required correction is for the rate of change of the ebullioscopic constant with

pressure at standard atmospheric pressure. This is obtained by eliminating the latent heat from (3.1) by using one of the approximate forms of the Clapeyron-Clausius equation[7]:

$$dp/dT = C_v p/RT^2 \tag{4.1}$$

C_v is the molar heat of vaporisation and is thus equal to $c_v M$, where M is the molecular weight of the solvent and c_v is the heat of vaporisation per g. Hence

$$K = pM/1000 \cdot dT/dp \tag{4.2}$$*

The rate of change of the ebullioscopic constant with pressure, expressed as a percentage, is given by $100/K \cdot dK/dp$. Now

$$\begin{aligned} 100/K \cdot dK/dp &= 100/K \cdot dK/dT \cdot dT/dp \\ &= 10^5/pM \cdot dK/dT, \text{ substituting from (4.2)} \end{aligned} \tag{4.3}$$

If the vapour pressure–temperature relationship of the solvent is expressed by means of the Antoine equation[13]

$$\log_{10} p = A - B/(C + t) \tag{4.4}$$

where p is in mm Hg and t is in °C, differentiation gives

$$dt/dp = (C + t)^2/2.303Bp \tag{4.5}$$**

Hence, since dT/dp and dt/dp are equivalent, substitution in (4.2) gives

$$K = M(C + t)^2/2303B \tag{4.6}$$

which by differentiation gives

$$dK/dt = 2\,M(C + t)/2303B \tag{4.7}$$

Substitution for dK/dt ($\equiv dK/dT$) in (4.3) gives

$$100/K \cdot dK/dp = 86.9(C + t)/Bp \tag{4.8}$$

which reduces at the standard atmospheric pressure of 760 mm to

$$100/K \cdot dK/dp = 0.115(C + t)/B = c_1 \tag{4.9}$$

The correction term c_1, *i.e.* the percentage change in ebullioscopic constant for 1 mm change in pressure at standard atmospheric pressure, is calculated in Table I for a representative range of ebullioscopic solvents. The Antoine constants given in the Table for the non-aqueous solvents[13] and water[14] are suitably rounded off.

* (4.2) has been derived from first principles by some authors[10,11] and is indeed considered by HOYT AND FINK[12] to be preferable to (3.1) for calculating the ebullioscopic constant, since R, which they claim should be corrected by the Berthelot equation, has been eliminated.

** This is differentiated erroneously as $\log_{10} C(C + t)^2/Bp$ by KITSON AND MITCHELL[5], presumably because of typographical confusion with $\log_{10} e(C + t)^2/Bp$.

TABLE I

CORRECTION TERM FOR THE EFFECT OF VARIATIONS IN BAROMETRIC PRESSURE ON THE EBULLIOSCOPIC CONSTANT

Solvent	*Boiling point* °C	*Antoine constants*		*Correction term* $c_1 = 0.115(C + t)/B$ %
		B	*C*	
Acetone	56.2	1233	230	0.0265
Carbon tetrachloride	76.7	1245	230	0.0282
Ethanol	78.3	1653	230	0.0214
Benzene	80.1	1206	220	0.0285
Water	100.0	1648	226	0.0226
Toluene	110.6	1344	219	0.0281
Chlorobenzene	131.7	1557	230	0.0266
Dioxan[a]	$T = 373$°K	$B' = 1867$		0.023

[a] Since the Antoine constants are not known for dioxan, the more approximate vapour pressure–temperature relationship:

$$\log p = A' - B'/T \text{ (where } T \text{ is in °K)} \tag{4.10}$$

is used, leading to the analogous expression

$$100/K \cdot \mathrm{d}K/\mathrm{d}p = 0.115\ T/B' \tag{4.11}$$

Although the correction term has been calculated at standard atmospheric pressure, it may be used with negligible error for pressures in the vicinity of 1 atmosphere; *e.g.* for variations of ±40 mm in pressure it can be shown from (4.8) that, by neglecting the slight change in t in comparison with the change in p, the correction term (which is itself small) varies by only ± 5% of its value at standard atmospheric pressure. This conclusion can be reached more rigorously by differentiating (4.8) again with respect to pressure and expressing it as a percentage, *viz.*:

$$100 \cdot \frac{\dfrac{\mathrm{d}}{\mathrm{d}p}\left(\dfrac{86.9(C+t)}{Bp}\right)}{\dfrac{86.9(C+t)}{Bp}} = \frac{100}{p}\left(\frac{C+t}{2.303B} - 1\right) \tag{4.12}$$

Substitution of the values for the Antoine constants and boiling point of, *e.g.*, benzene gives a percentage change with pressure of —0.12% per mm in the percentage change of ebullioscopic constant with pressure, agreeing with the value of 5% per 40 mm obtained above.

The tabulated values, when converted from percentage to actual corrections, are slightly higher than those generally given in the tables of ebullioscopic constants to be found in the reference books, since the latter values are generally those calculated by HOYT AND FINK[12]; these authors neglect to take into account the variation of latent heat of vaporisation with temperature and their values are correspondingly slightly low. For example they give for carbon tetrachloride $K = 5.03°$ per mole for 1000 g solvent with a barometric correction of 0.0013° per mm, whereas the correction term of 0.0282% per mm in Table I is equivalent to a correction of 0.0014° per mm. The difference caused by their error is obviously negligible for all practical purposes. The tabulated value for benzene agrees well with the value of 0.029% per mm at 760 mm derived from the ebullioscopic constants for benzene over the range 740–780 mm calculated recently from very accurate vapour pressure and thermal data[15].

(b) The correction term for the effect of variations in barometric pressure on the sensitivity of the Menzies differential thermometer

The required correction is for the rate of change of thermometer sensitivity with pressure at the temperature corresponding to the boiling point of the given ebullioscopic solvent. This, expressed as a percentage of the sensitivity at that temperature, is equal to the product of the percentage rate of change of thermometer sensitivity per ° change in temperature at the boiling point of the ebullioscopic solvent and the rate of change of boiling point of the ebullioscopic solvent per 1 mm Hg change in pressure at atmospheric pressure, *viz.* $100d/dt(dt/dp)_f/(dt/dp)_f \cdot (dt/dp)_s$, where the subscripts f and s denote the thermometer filling liquid and the ebullioscopic solvent respectively. By differentiating (4.5) this reduces to

$$200(C + t - 1.152B)/(C + t)^2 \cdot (dt/dp)_s = c_2 \qquad (4.13)$$

where B and C are the Antoine constants of the filling liquid and t is the boiling point in °C of the ebullioscopic solvent; $(dt/dp)_s$ may be calculated from the Antoine constants of the ebullioscopic solvent using (4.5) or, more conveniently, may be taken from tables[13].

Values of the correction term c_2 (*i.e.* the percentage change in thermometer sensitivity for 1 mm change in pressure at standard atmospheric pressure), calculated for the relevant thermometer filling liquids at the temperatures corresponding to the boiling-points of the ebullioscopic solvents used in the extension of COLSON's semi-micro method[3], are given in Table II. Since $1.152B$ is greater than $C + t$ the correction term is negative in sign, *i.e.* although the sensitivity (expressed as mm/°C) increases with increase in pressure (equivalent to increase in temperature), it decreases when expressed reciprocally as the Menzies factor in °/mm.

TABLE II

CORRECTION TERM FOR THE EFFECT OF VARIATIONS IN BAROMETRIC PRESSURE ON THE SENSITIVITY OF THE MENZIES DIFFERENTIAL THERMOMETER

Solvent	*B.P.* °C	$(dt/dp)_s$ *at 760 mm Hg* °C/*mm*	*Benzene thermometer*		*Water thermometer*	
			$200\frac{(C + t - 1.152B)}{(C + t)^2}$ %	*Correction term,* c_2 %	$200\frac{(C + t - 1.152B)}{(C + t)^2}$ %	*Correction term,* c_2 %
Acetone	56.2	$3.80 \cdot 10^{-2}$	—2.92	—0.111	—4.07	—0.154
Carbon tetrachloride	76.7	$4.32 \cdot 10^{-2}$	—2.48	—0.107	—3.47	—0.150
Ethanol	78.3	$3.34 \cdot 10^{-2}$	—2.46	—0.082	—3.44	—0.115
Benzene	80.1	$4.27 \cdot 10^{-2}$	—2.42	—0.103	—3.38	—0.145
Dioxan	101.3	$4.32 \cdot 10^{-2}$	—	—	—2.95	—0.127
Toluene	110.6	$4.63 \cdot 10^{-2}$	—	—	—2.76	—0.128
Chlorobenzene	131.7	$4.88 \cdot 10^{-2}$	—	—	—2.52	—0.123

Although the tabulated values of the correction terms c_2 are strictly correct only at atmospheric pressure, they may be used without significant error over the range 720–780 mm. Thus the percentage change in c_2 with pressure is equal to the sum of the percentage changes with pressure in each of the terms $(dt/dp)_s$ and $200(C + t - 1.152B)/(C + t)^2$. These are found by differentiating with

respect to p to be respectively $100/p \cdot [(C + t)/1.152B - 1)]$ and $43.4(C + t)/Bp \cdot [2.303B - (C + t)]/(C + t - 1.152B)$, reducing at atmospheric pressure to $0.132 [(C + t)/1.152B - 1)]$ and $0.0572(C + t)/B \cdot [2.303B - (C + t)]/(C + t - 1.152B)$. Substitution for a typical set of conditions, *e.g.* benzene as ebullioscopic solvent with a benzene-filled thermometer, gives the percentage changes as respectively —0.103% per mm and —0.032% per mm; the total percentage change in c_2 with pressure is thus —0.135% per mm, this being due mainly to the change in dt/dp with pressure consequent upon the logarithmic form of the vapour pressure – temperature relationship for liquids. Thus for a change in pressure of 40 mm the percentage change in c_2 is 5.4%; this is insignificant because c_2 itself is small. The same argument applies to all the solvent-filling liquid combinations examined.

(c) Combination of the percentage correction terms c_1 and c_2 into a single comprehensive term

Let the barometric pressure (corrected) $= b$ mm Hg. Then, substituting in (3.5) and denoting the barometric pressure by subscripts,

$$\frac{K'_b}{K'_{760}} = \frac{K_b}{K_{760}} \Big/ \frac{f_b}{f_{760}}$$

$$= \frac{1 + (b - 760)c_1/100}{1 + (b - 760)c_2/100}$$

$$\simeq 1 + (b - 760)(c_1 - c_2)/100, \text{ since } c_1 \text{ and } c_2 \text{ are both small.} \qquad (4.14)$$

Let $(c_1 - c_2)/100 = F$. Then if a mass m causes an elevation of boiling point ΔT, K'_b and K'_{760} can be replaced respectively by the proportional expressions $\Delta T/m$ (determined on a given ebulliometer at barometric pressure b mm) and Y (the value of $\Delta T/m$ corrected to standard atmospheric pressure), leading to

$$Y = \Delta T/m/[1 + F(b - 760)] \qquad (4.15)$$

Values of F, calculated from the values of c_1 in Table I and c_2 in Table II, are collected in Table III. They are given to only 2 significant figures since the third figure is insignificant.

TABLE III

COMPREHENSIVE CORRECTION TERM FOR THE EFFECT OF VARIATIONS IN BAROMETRIC PRESSURE ON EBULLIOSCOPIC DETERMINATION OF MOLECULAR WEIGHT USING THE MENZIES DIFFERENTIAL THERMOMETER

Ebullioscopic solvent	F *Benzene thermometer*	F *Water thermometer*
Acetone	$1.4 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$
Carbon tetrachloride	$1.4 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$
Ethanol	$1.0 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$
Benzene	$1.3 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$
Dioxan	—	$1.5 \cdot 10^{-3}$
Toluene	—	$1.6 \cdot 10^{-3}$
Chlorobenzene	—	$1.5 \cdot 10^{-3}$

APPLICATION OF THE COMPREHENSIVE CORRECTION TERM IN THE EBULLIOSCOPIC DETERMINATION OF MOLECULAR WEIGHT

The determination of molecular weight by COLSON's methods[2] and the extension thereof[3] simply consists of determining $\Delta T/m$ (in mm/mg) for both the sample and the standard compound in a fixed volume of an appropriate solvent, correcting these to the values Y at standard atmospheric pressure (using 4.15 and Table III), and, from the inverse relationship between Y and molecular weight, calculating the molecular weight of the sample, given the molecular weight of the standard.

For laboratories where the prevailing barometric pressure is much different from 760 mm, *e.g.* those at high altitudes, the necessary correction to standard atmospheric pressure to be applied may be 10% or more, and the approximations made in the above treatment leading to the values in Table III may become significant. It is then preferable to correct the results to a standard pressure other than 760 mm; this pressure should be the approximate mid-point of the pressure range encountered. Table III should then be recalculated using the equations developed above.

EXPERIMENTAL VERIFICATION OF THE COMPREHENSIVE CORRECTION TERM

The validity of the comprehensive correction term for the combination of benzene as ebullioscopic solvent with the benzene-filled differential thermometer was investigated by carrying out a series of 39 standardization experiments in a semi-micro ebulliometer; the solute was the standard compound benzil (mol. wt. 210) and the fixed volume of benzene was 10 ml. These experiments were performed at irregular intervals over a 12-month period at barometric pressures ranging from 717 to 778 mm Hg (mean 751 mm Hg). The uncorrected values $\Delta T/m$ showed considerable scatter, with a range of 573 to 640 mm/g, a mean of 605 mm/g and a coefficient of variation of 2.3%, whereas the corrected values Y (using equation 4.15 with $F = 1.3 \cdot 10^{-3}$ from Table III) showed less scatter, with a range of 595 to 626 mm/g, a mean of 612 mm/g and a coefficient of variation of 1.3%. Further statistical analysis gave the following equations for the regression of respectively the uncorrected and corrected values on barometric pressure, where $\Delta T/m$ and Y are in mm/g and b in mm Hg:

(*a*) *Uncorrected values*

Regression equation: $\Delta T/m = 605 + 0.744(b - 751)$. Standard error of the regression coefficient: 0.080. 95% confidence limits of the regression coefficient: 0.58 to 0.91.

(*b*) *Corrected values*

Regression equation: $Y = 612 - 0.067(b - 751)$. Standard error of the regression coefficient: 0.081. 95% confidence limits of the regression coefficient: —0.23 to 0.10.

The analysis consequently shows that the dependence of the uncorrected values on pressure is highly significant, whereas that for the corrected values is not significant, thus verifying the validity of the comprehensive correction term.

ACKNOWLEDGEMENTS

I should like to thank DR. F. R. CROPPER for helpful criticism and MR. A. HEDLEY for experimental assistance.

SUMMARY

A theoretical treatment of the effect of variations in barometric pressure and other factors on the ebullioscopic determination of molecular weights leads to general expressions relating the variations in barometric pressure with the ebullioscopic constant of the solvent and with the temperature sensitivity of the MENZIES differential thermometer. Since these variations can affect significantly the accuracy of ebullioscopic molecular weight determinations, a single comprehensive correction term is calculated for each of the usual combinations of ebullioscopic solvent and thermometer filling liquid; this term enables results obtained at different pressures to be corrected to standard atmospheric pressure, thus eliminating the pressure effect. Finally a statistical analysis of some experimental results illustrates the validity of the correction term for the combination of benzene as ebullioscopic solvent with benzene as thermometer filling liquid.

RÉSUMÉ

L'auteur a examiné l'influence des variations de la pression barométrique, ainsi que d'autres facteurs, sur la détermination des poids moléculaires par ébullioscopie (avec utilisation du thermomètre différentiel MENZIES).

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über den Einfluss des Luftdruckes sowie anderer Faktoren auf die ebullioskopische Molekulargewichtsbestimmung mit dem Differentialthermometer nach MENZIES.

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APPLICATION OF THE DOUBLE WITHDRAWAL COUNTERCURRENT EXTRACTION TECHNIQUE TO ANALYTICAL CHEMISTRY

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Although fractional solvent extraction and countercurrent distribution have been used for numerous chemical engineering processes, the use of the countercurrent distribution technique in chemical analysis has been primarily limited to what CRAIG classifies as the "fundamental" countercurrent extraction process[1]. The "double withdrawal" process[2] would be of much greater interest and utility to the practicing analyst, but has unfortunately been largely neglected. Probably the major reason for its limited usage is the staggering complexity of the mathematics associated with the process. Before attempting to build an apparatus suitable for automatic operation, some knowledge of possible results from the use of the process is desirable. The manual performance of this extraction technique, with more than a few stages, is obviously out of the question.

A search of the literature has revealed only one attempt to solve the mathematics associated with the double withdrawal countercurrent extraction process. COMPERE AND RYLAND[3] attacked the problem through the probability concept of the random walk and presented results calculated for several cases. However, this method of calculation is quite difficult and is an obstacle of sufficient prominence to prevent consideration of the method in the laboratory.

The writer preferred to attack the problem by means of present day computer technology so that results could be obtained rapidly for several conditions in order to determine whether or not the process was of analytical interest. Although the double withdrawal process has been described elsewhere[2,3], a brief description here seems advisable in order to clarify the terms to be used.

The double withdrawal extraction pattern is shown in Fig. 1 and is similar to that shown by COMPERE AND RYLAND. Each circle represents an extraction container, such as a separatory funnel. For purposes of simplicity, we shall consider what happens to only one material. The material under consideration is fed into the first container (C) as indicated and the solvent volumes are adjusted so that there are equal volumes of each phase. For simplicity of treatment, all phase ratios will be adjusted to unity. The mixture is shaken and allowed to separate. The heavy phase is drained and transferred to tube R1 as indicated, and the light phase is transferred to tube L1. This is called the first extraction, or $n = 1$. Heavy solvent is added to tube L1 and light solvent is added to tube R1. These two mixtures are shaken and allowed to separate. The heavy solvent in L1 is transferred to C and the light solvent in L1 is transferred to L2. Similarly, the heavy solvent in R1 is transferred to R2 and the light solvent

transferred to C. This is the second extraction, or $n = 2$. Heavy and light solvents are added to L2 and R2 respectively and the three mixtures are shaken and allowed to separate. The heavy solvent in R2 and light solvent in L2 are withdrawn as products. The heavy solvents in C and L2 are transferred to R1 and L1 respectively. The light solvents in C and R2 are transferred to L1 and R1 respectively. This is the third extraction, or $n = 3$. This procedure is carried on for any number of extractions desired. It will be noticed that light and heavy products are obtained after every other extraction, and that appropriate solvent must be added as indicated. The system shown in Fig. 1 is considered as having five stages ($S = 5$). It can be shown that the

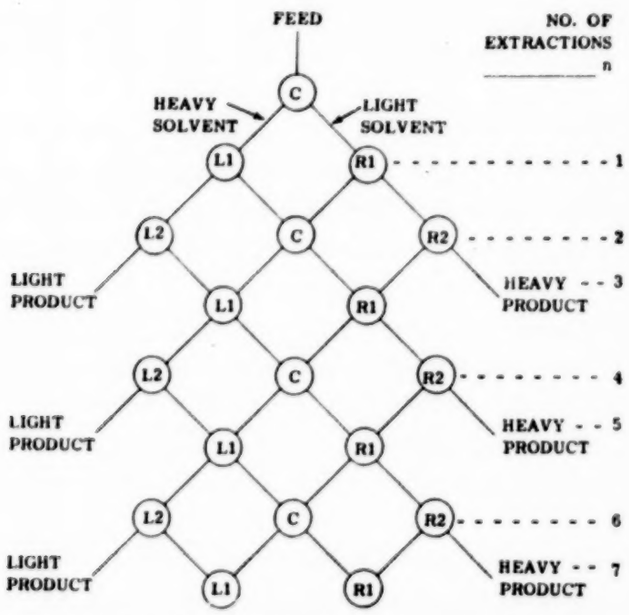

Fig. 1. Double withdrawal extraction pattern.

first portion of product is obtained after $(S + 1)/2$ extractions, where S designates the number of stages. If we assume that the fraction of the material transferred to the heavy solvent after one extraction is α, and the fraction transferred to the light solvent is β it can be shown that for five stages, the total amount of material collected in the heavy solvent product after 3 extractions is α^3, after 5 extractions it is $\alpha^3 + 3\alpha^4\beta$, after 7 extractions it is $\alpha^3 + 3\alpha^4\beta + 9\alpha^5\beta^2$, etc. It can also be shown that the total amount collected (again considering only the heavy solvent product) may be represented by

$$Q = M(A\alpha^r + B\alpha^{r+1}\beta + C\alpha^{r+2}\beta^2 + D\alpha^{r+3}\beta^3 + \ldots)$$

where S = number of stages, $r = (S + 1)/2$, Q = total amount of material collected, M = amount of material originally present, α = weight fraction of material extracted into heavy solvent in one extraction, β = weight fraction of material extracted into light solvent in one extraction, and $\alpha + \beta = 1$. A,B,C,D, etc., are coefficients. The number of coefficients to be used and the value of each coefficient is determined by the number of stages and the number of extractions performed. Initially, it would appear that some simple relationship exists for these coefficients. For example, for $S = 5$, the values of the coefficients are 1,3,9,27,81, etc. For $S = 3$, the values are 1, 2, 4, 8, 16, 32, 64, etc. Thus, for 3 or 5 stages, the coefficients are a function of $[(S+1)/2]^n$.

However, when $S = 7$, the values for these coefficients are 1, 4, 14, 48, 164, 560, etc. Likewise, for $S = 9$, the coefficients are 1, 5, 20, 75, 275, 1000, etc., for $S = 11$, the coefficients are 1, 6, 27, 110, 429, etc. A careful examination of these coefficients has led to the conclusion that no simple relationship exists between them.

It therefore seemed appropriate to use the International Business Machine 704 Computer to solve for and store coefficient values for different combinations of S and n. This was done for odd values of S from 3 through 101; also for $S = 111$, 121, 131, 141, 151, 161, 171, 181, 191, 201, 221, 241, 261, 281, 301, 351, 401, 501, 601, 701, 801, and 1001. Coefficients were obtained for each of the preceding values of S for up to 600 extractions, or until the machine could no longer handle the data. To indicate the order of magnitude of some of the coefficients, values of 10^{140} are not uncommon.

After the coefficients had been stored, the total products for values of $\alpha = 0.01$, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 0.95, 0.98, and 0.99 were obtained for a number of different stages and extractions. The machine carried on the problem solution until essentially all of the material was removed from the system, or until the machine limitations were reached. The computer was programmed to stop before giving incorrect answers. The computer program used in this work is indicated later.

The information obtained is shown plotted in Figs. 2–9 as total percent extracted

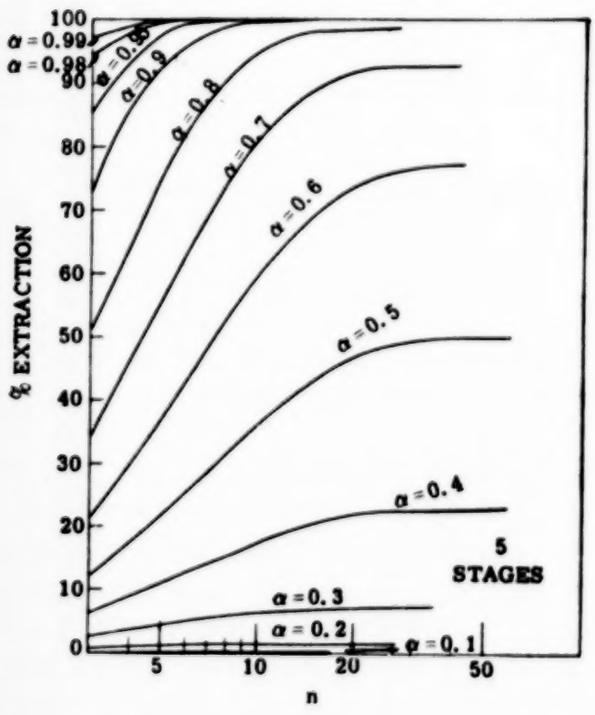

Fig. 2. Theoretical double withdrawal recoveries with 5 stages.

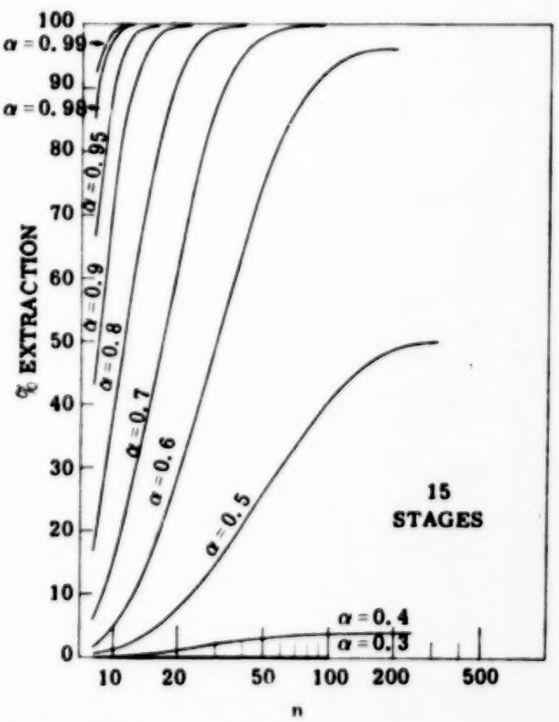

Fig. 3. Theoretical double withdrawal recoveries with 15 stages.

(for various values of α) *vs.* the number of extractions. Several points should be remembered while considering these curves. First, in a separation of two materials, x and y, where for example, $\alpha_x = 0.9$ and $\alpha_y = 0.7$, the material having a value of $\alpha = 0.9$ will appear first in the product. Assuming that the separation is done automatically and that there are both kinds of solvent in all the tubes, solvent will be collected containing separated material on alternate values of n. Note that separated

material is not obtained until $(S + 1)/2$ extractions, therefore the material has been diluted much less than it would seem.

The amount extracted for values of α not shown in the figures is essentially zero

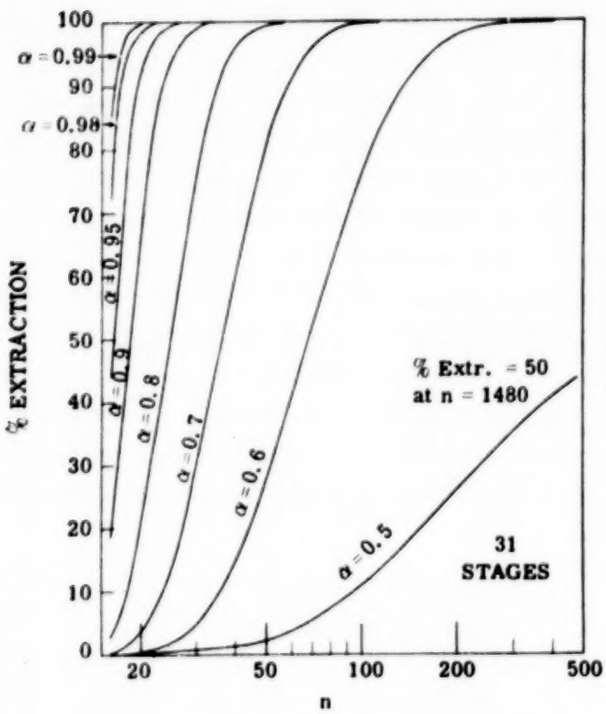

Fig. 4. Theoretical double withdrawal recoveries with 31 stages.

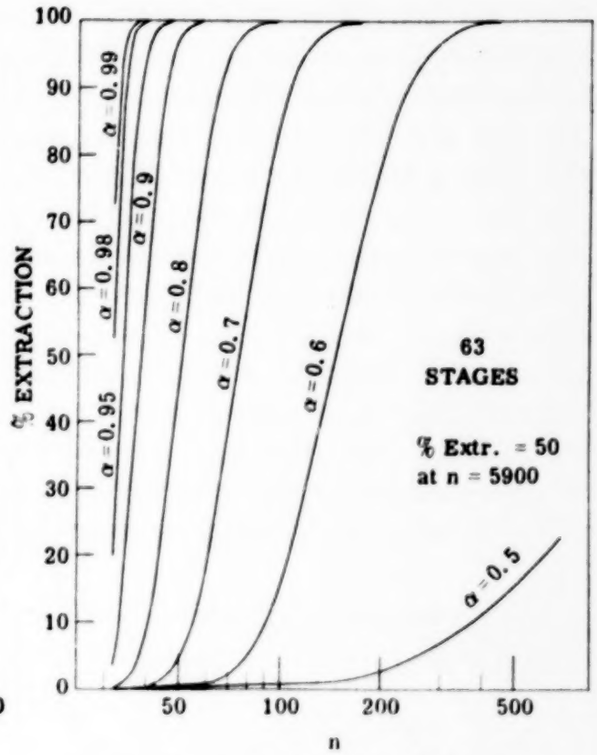

Fig. 5. Theoretical double withdrawal recoveries with 63 stages.

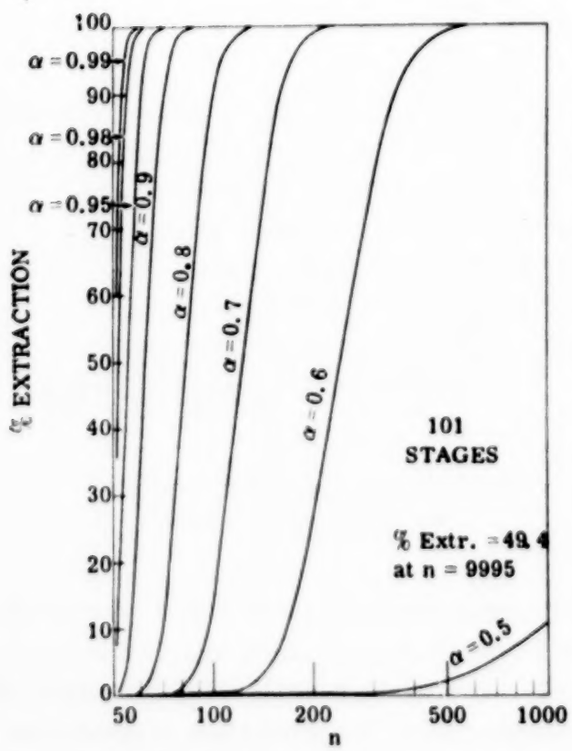

Fig. 6. Theoretical double withdrawal recoveries with 101 stages.

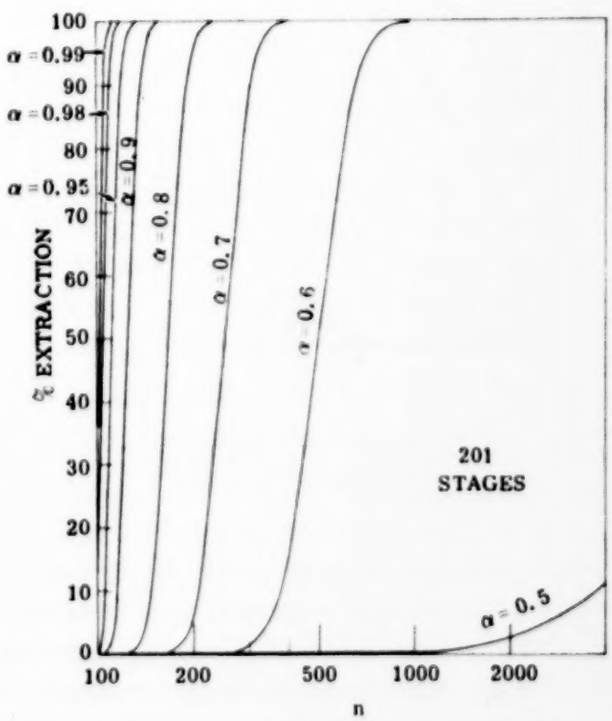

Fig. 7. Theoretical double withdrawal recoveries with 201 stages.

for the range of extractions covered. It should be noted that only the material obtained in the heavy solvent product is considered. (The amount collected in the light product will of course be the same as that collected in the heavy product for $1 - \alpha$).

Examination of Figs. 2–9 indicates that the double withdrawal process has some very interesting analytical possibilities. To illustrate the advantage of this procedure over the direct extraction technique, let us compare the separation of two substances, x and y, where $\alpha_x = 0.9$ and $\alpha_y = 0.3$. If we start with equal amounts of x and y, and a phase ratio of unity, after one extraction using the direct extraction technique, the amounts of x and y in the extract would be 90% and 30% of the original amount

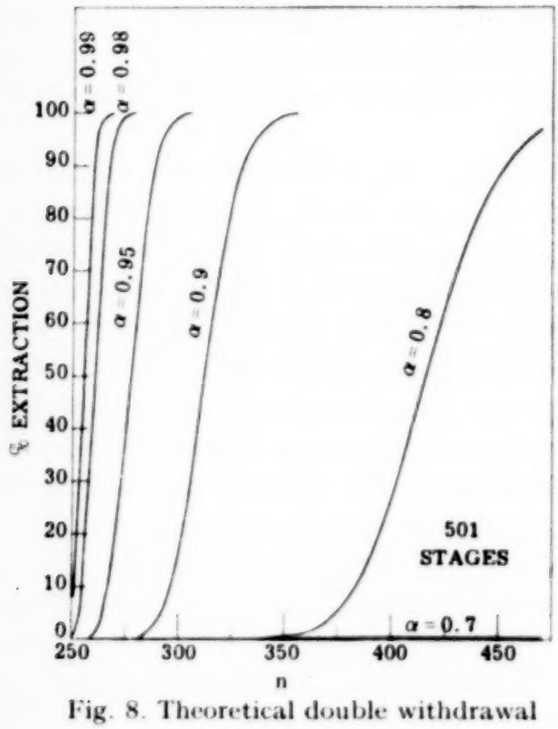

Fig. 8. Theoretical double withdrawal recoveries with 501 stages.

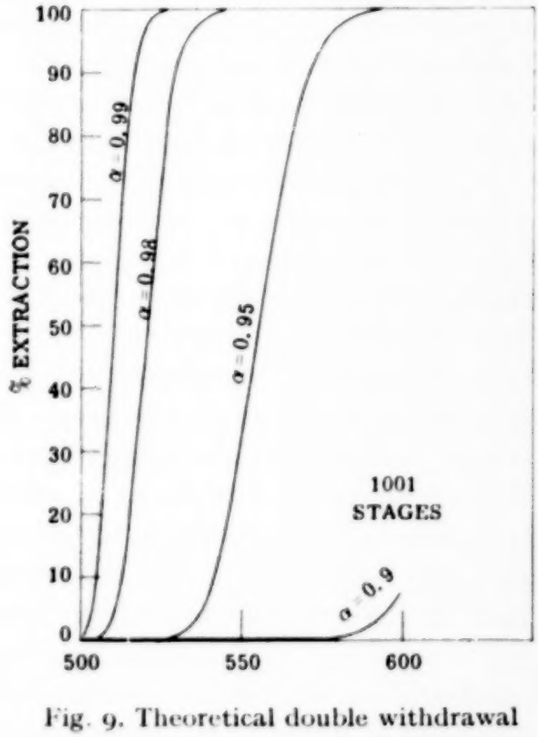

Fig. 9. Theoretical double withdrawal recoveries with 1001 stages.

respectively. If we desire for analytical purposes to recover at least 99% of the amount initially present, another extraction must be made of the original phase which contained the material to be separated. This time we obtain 9% of material x (90% of 10%), and 21% of material y (30% of 70%). We now have recovered 99% of x and the purity of our material (with respect to x) has improved from an original 50% to 66%. Table I indicates recovery and purity data for the separation of x and y for two different cases. Note that as the percent recovery increases, the purity decreases.

TABLE I

RECOVERY AND PURITY BY DIRECT EXTRACTION TECHNIQUE

n	$\alpha_x = 0.9$; $\alpha_y = 0.3$		$\alpha_x = 0.9$; $\alpha_y = 0.7$	
	% *Recovery (x)*	% *Purity (x)*	% *Recovery (x)*	% *Purity (x)*
1	90	75	90	56.2
2	99	66	99	52.1
3	99.9	60.5	99.9	51.6
4	99.99	56.8	99.99	51.2

It is obvious from Table I that the direct extraction technique is relatively useless for analytical separations unless the distribution coefficients of the materials to be separated are considerably different.

In contrast to the direct extraction technique, Fig. 3 indicates that after 22 extractions using the countercurrent technique and 15 stages, 99.9% of x would be recovered essentially 99.9% pure when $\alpha_x = 0.9$ and $\alpha_y = 0.3$. If we assume a volume of 10 ml for each phase, the total amount of solvent which contained material x would be (220 — 80)/2 or 70 ml.

Fig. 7 indicates that after 155 extractions with 201 stages, 99.9% of x is again recovered essentially 99.9% pure when $\alpha_x = 0.9$ and $\alpha_y = 0.7$. Note that the volume containing x is (1550–1000)/2 or 275 ml, again assuming initial phase volumes of 10 ml. Furthermore, lest 201 stages seems to be of theoretical value only, the reader is referred to the work of CRAIG in which 1000-cell countercurrent distribution instruments have been used for automatic separations.

Figs. 2–9 are obviously not all-inclusive; the values of α and S were selected to give a reasonable amount of information and still meet the usual space requirements. Careful examination of the figures will indicate the applicability of the double withdrawal countercurrent technique to chemical analysis. In Fig. 2 for example, quantitative recovery (99.9%) is obtained, using 5 stages, only for material having α equal to or greater than approximately 0.9. For lower values of α, somewhat less than 100% recovery is obtained (in the heavy solvent product); the remainder of the material is obtained in the light solvent product. The figures have been drawn to indicate either essentially complete removal of material from the system, or to indicate computer limitations. When the curve asymptotically approaches the horizontal, one may assume complete removal from the system. The curves shown in Fig. 2 also indicate that a quantitative separation of material having α equal to (or greater than) 0.9 is obtained only from material having α equal to approximately 0.1 to 0.2 (depending upon exactly what is meant by the word quantitative). The curves in Figs. 3–9 can be interpreted in the same manner.

Examination of the figures indicates the possible separations which might be made, depending upon the distribution coefficients involved. The closer the distribution coefficients of the materials to be separated are to each other, the greater the number of stages needed for extraction. It is quite interesting to note however, that the material desired will be collected in a volume which will not prohibit use of the usual analytical methods.

The following assumptions are of course implicit in the foregoing treatment:

1. The distribution coefficients are independent of concentration.
2. Equilibrium is assumed to have occurred for each extraction.
3. Complete separation and transfer of the phases occurs with no solvent loss by evaporation.
4. The phases are immiscible, or can be pre-equilibrated.
5. No chemical interaction or phase inversion occurs.

The foregoing data have indicated the application of the double withdrawal countercurrent extraction technique to chemical analysis. Work is proceeding to test this type of separation experimentally, the final objective being the development of an automatic apparatus. It is hoped that this article will stimulate sufficient interest among analysts to warrant other experimental investigations.

COMPUTER PROGRAM

For persons interested in obtaining results not included in this report, a program has been written for the International Business Machine 704 computer which will compute, for a given number of stages, either (1), the coefficients $A, B, C, D, \ldots$ or (2), for a given value of α, the quantity Q collected in either solvent product as a function of $A, B, C, D, \ldots$ on the assumption of a unit mass originally introduced into the middle stage. In both cases the coefficients $A, B, C, D, \ldots$ are generated by the following scheme, shown for illustrative purposes with 13 stages:

1	1	1	1	1	1	1	0
2	3	4	5	6	7	7	0
6	10	15	21	28	35	35	0
20	35	56	84	119	154	154	0
70	126	210	329	483	637	637	0
252	462	791	1274	1911	2548	2548	0
924	1715	2989	4900	7448	9996	9996	0
.	.	.	.	.	.	.	.

The first column corresponds to the middle (7th) stage and the second column from the right contains the coefficients $A, B, C, D, \ldots$ If $\gamma_{i,j}$ denotes the number in the i-th row and j-th column, the $\gamma_{i,j}$'s are generated recursively as follows:

$$\gamma_{1,j} = 1 (j = 1, 2, \ldots, r); \gamma_{1,r+1} = 0$$

$$\gamma_{i,1} = 2\gamma_{i-1,2} (i = 2, 3, \ldots)$$

$$\gamma_{i,j} = \gamma_{i,j-1} + \gamma_{i-1,j+1} (j = 2, 3, \ldots, r; i = 2, 3, \ldots)$$

Hence

$$\gamma_{1,r} = A, \gamma_{2,r} = B, \gamma_{3,r} = C, \text{ etc.};$$

in the example,

$$\gamma_{1,7} = A = 1, \gamma_{2,7} = B = 7, \gamma_{3,7} = C = 35, \text{ etc.}$$

Since a number equal to or greater than 2^{128} cannot be represented in the computer, the rows occurring in this generation scheme may need to be scaled several times to keep the numbers within the proper range. (When printed out, the coefficients A, B, C, D, ... and the quantities Q are rescaled). However, if the ratio $\gamma_{i,r}/\gamma_{i,1}$ ever exceeds 2^{128}, as may happen with large values of S, the machine limitations are exceeded and the computations cease. Results so far indicate that this condition will occur for values of S greater than about 300. This does not mean that the program is not valid for values of S greater than 300; it only indicates that one might not be able to obtain as many coefficients or extractions as is desired. This is especially true for S much greater than 300 or for α near to 0.5. With this exception, a specified number of coefficients or extraction quantities may be computed for any value of S. The computer may be asked to stop computations after a specified percent recovery.

More explicit directions will be supplied if the program itself is requested.

ACKNOWLEDGEMENTS

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med the International Business Machine 704 computer and obtained the numerical results which are the basis for this presentation. The author feels considerably indebted to J. A. McGURTY for his support of this program and to H. S. EDWARDS for his recommendations concerning presentation.

SUMMARY

Application of the double withdrawal countercurrent extraction technique to chemical analysis has been singularly neglected, probably because of the complexity and tediousness of the associated mathematics. Present day computer technology proved to be readily applicable to the problem and information is presented which indicates the possible importance of this separation method to chemical analysis.

RÉSUMÉ

L'auteur décrit l'emploi d'un "computer" pour le traitement mathématique des procédés d'extraction à contrecourant, avec double prélèvement. Il démontre l'importance de ce procédé pour l'analyse chimique.

ZUSAMMENFASSUNG

Es wird über die Anwendung der "Computer" zur mathematischen Behandlung des Gegenstrom-Extraktionsverfahrens mit doppelter Entnahme berichtet. Auf die Bedeutung des Verfahrens für chemische Analysen wird hingewiesen.

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TITRIMETRIC METHODS FOR THE MICRODETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS BY THE RAPID COMBUSTION PROCEDURE

I. THE DETERMINATION OF INDIVIDUAL HALOGENS

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INTRODUCTION

Several titration procedures for the microdetermination of the halogens (chlorine, bromine and iodine) in organic compounds were outlined in the original communication to this journal on the rapid, empty tube combustion procedure[1]. In a more recent paper, INGRAM[2] has suggested that for daily routine analysis potentiometric titration is preferable to other titration procedures for the evaluation of the halogens. However, it may not always be convenient to use this method, and if non-instrumental methods are equal in speed and accuracy they are generally to be preferred. Other acid-producing elements, such as nitrogen and sulphur, which often occur in organic combination with one or more of the halogens, can influence considerably the type of absorbent required for a particular halogen. The choice of the final titrimetric procedure is influenced by the absorbent used.

Because several important aspects of these methods were not fully discussed in the earlier publications[1-3], it is proposed to present a short series of papers describing the results of later experience and of a study[4] on various titrimetric procedures suitable for the microdetermination of the halogens in all their possible organic combinations with oxygen, nitrogen, sulphur and with each other.

DISCUSSION

Halogens in the absence of nitrogen and sulphur

The combustion products from these halogenated organic compounds consist almost exclusively of carbon dioxide, water vapour and the free halogen. It is unlikely that hydrogen halides can be formed, for at the elevated temperatures of this combustion complete oxidation is to be expected. Chlorine and bromine were originally absorbed in neutral hydrogen peroxide which allowed a direct acidimetric titration to be used. The reactions of iodine with hydrogen peroxide are, however, too complex to be dependable, and absorption in strong alkali or bisulphite or both is generally preferred.

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Halogens in the presence of nitrogen

The mechanisms involved in the destructive oxidation of nitrogenous substances by the rapid combustion method have not been fully elucidated. INGRAM[5] has shown that in addition to the free halogen, water vapour and carbon dioxide, both elemental nitrogen and oxides of nitrogen are produced in varying amounts depending on the nature of the original nitrogen linkage. Calculations from available thermodynamical data indicate that the prevailing conditions do not favour any appreciable additional oxidation of the elemental nitrogen to nitric oxide[4]. INGRAM found that most types of nitrogenous compound produce relatively small amounts of nitric acid when their combustion products are absorbed in a neutral hydrogen peroxide solution, but nitro compounds, not unexpectedly, give a high rate of conversion to nitrogen dioxide. In most cases the quantity of nitric acid formed prevents the direct acidimetric titration of the halogen acid.

Halogens in the presence of sulphur

When organic compounds containing sulphur are burned, the experimental evidence suggests that the sulphur is converted initially to sulphur dioxide. It is most unlikely that further oxidation of the sulphur dioxide to the trioxide would occur; it is well established that sulphur trioxide undergoes dissociation to the dioxide very readily at moderately high temperatures. At the cooler exit-end of the combustion tube, however, conditions favour oxidation to the trioxide; unless the outlet is kept warm, appreciable condensation of sulphuric acid occurs at this point.

It is also possible under the prevailing conditions for chlorine and sulphur dioxide to react to yield sulphuric acid and hydrogen chloride[4,6]. When the products of combustion from various sulphur- and chlorine-containing compounds were collected in a liquid air trap and examined in the mass spectrometer it was found that β-sulphur trioxide was present in addition to carbon dioxide, sulphur dioxide and water[4]. No trace of any gaseous halogen derivative was found, but when the sulphur trioxide was dissolved in hydrogen peroxide, chloride ion was detected (84% of the original amount)[4]. Evidently this material had absorbed the hydrogen chloride[7]. No sulphuryl chloride or chlorosulphonic acid was found.

Conclusions on the composition of the breakdown products

The principal products are carbon dioxide, water vapour, the free halogens and, depending upon the original elemental composition of the compound, variable quantities of nitrogen, oxides of nitrogen and sulphur, nitric and sulphuric acids and hydrogen chloride. It is extremely unlikely that hydrogen bromide or iodide are formed in the gaseous state.

When the absorption media and titration procedures for the halogens are selected all the possible combustion products must be considered.

Some possible titrimetric methods for the halogens

Argentometric titrations have only been successfully applied to the microdetermination of the halogens by the rapid method when the end-point is detected potentiometrically. The mercuric oxycyanide method of VIEBÖCK[8] as modified by BELCHER, MACDONALD AND NUTTEN[9] has been found to be the most widely applicable visual

micro titration for the halogens; nitric and sulphuric acids do not interfere. Owing to the less favourable conversion factors, the titration of bromide or iodide is more exacting than that of chloride but, with care, results within the usual limits of accuracy can be obtained.

The most sensitive methods for the halogens are the amplification procedures which are based on the oxidation of the halide to the corresponding halate followed by an iodometric evaluation of the latter. Both the LEIPERT micro method[10] for iodine and the hypochlorite oxidation method of KOLTHOFF AND YUTZY[11] for bromine were found to give satisfactory results. Several indirect amplification procedures for chloride ions were examined by BELCHER AND GOULDEN[12], but they concluded that none was sufficiently accurate for microdeterminations.

The combustion products of bromine or chlorine compounds which do not contain nitrogen or sulphur can be absorbed in hydrogen peroxide solutions so that the halogen can be determined by an acidimetric titration.

Hydrogen peroxide solution as absorbent

The reaction kinetics of halogens with hydrogen peroxide have been studied extensively[4,13]. The reactions with bromine and chlorine are similar, each halogen being reduced to the corresponding halide under the conditions used. The reactions of iodine with peroxide depend on the medium[4,14,15]: in acid solution an almost quantitative oxidation to iodate occurs, but in alkaline solution there is complete reduction to iodide. In our attempts to exploit this reaction we were able to show that iodide ions were formed quantitatively during the alkaline peroxide absorption, but the iodide values obtained by direct acidimetric titration were very variable[4]. Hence, this titration procedure cannot be recommended for the determination of iodine.

Neutral hydrogen peroxide is usually a satisfactory absorbent for chlorine and bromine but it is less efficient than alkaline peroxide in the rapid combustion method; when compounds containing large amounts of bromine and, to a smaller extent, chlorine, are burnt, some slip occurs with neutral solutions. It is recommended, therefore, that alkaline hydrogen peroxide solutions always be used.

Alkaline bisulphite solution as absorbent

This solution can be used for the absorption of all three halogens. When two or more halogens are present it is to be preferred to hydrogen peroxide which may initiate a series of interfering side reactions[4]. However, alkaline peroxide is preferable when only one halogen has to be absorbed and the mercuric oxycyanide titration is used; hydrogen peroxide need not be removed whereas sulphur dioxide must be completely expelled.

Absorption of iodine

It was stated earlier that when alkaline hydrogen peroxide is used for absorption of iodine, direct acidimetric titration is not possible. The mercuric oxycyanide procedure can be applied since iodide is formed quantitatively, but the LEIPERT method is to be preferred. With the former method great care is necessary in the titration because of the unfavourable conversion factor; even when sample weights of 8–12 mg are used, the titrant must be measured to ± 0.015 ml to obtain the required accuracy. This procedure only finds application in the special case where the other halogens

are present and their total amount has to be determined; the experimental details are exactly the same as for the determination of chlorine and bromine with the important exception that hydrogen peroxide must be completely destroyed (by means of a platinum-black destructor rod) before acidification.

The well-known LEIPERT procedure with its six-fold amplification should be applied whenever possible. INGRAM recommended an acetic acid–sodium acetate buffered solution of bromine as absorbent[3]. We prefer sodium hydroxide solution for this purpose to avoid the bromine fumes; it is important, however, to avoid high electrolyte concentrations which decrease the sensitivity of the starch end-point. We also prefer phosphoric to acetic acid for neutralising the excess of alkali; it is not then necessary to add acetic acid–sodium acetate buffer because the solution is buffered sufficiently by the sodium phosphate produced in the neutralisation. The total electrolyte concentration is thus reduced to about one-half of the usual amount.

EXPERIMENTAL

A. Determination of chlorine or bromine (in absence of N and S)

Indicators

(1) Screened methyl red–methylene blue indicator solution. Prepare separate solutions of 0.125 g of methyl red in 50 ml of 90% ethanol and 0.083 g of methylene blue (redox purity) in 50 ml of 90% ethanol, and mix equal volumes of the two solutions immediately before use. *(2)* Aqueous methyl red indicator solution.

Procedure

Burn the sample as described in the earlier paper[1] using as absorption solution an exactly measured volume of 0.01 *N* sodium hydroxide (*ca.* 10 ml), together with a known volume of 30% hydrogen peroxide (0.5–1.0 ml) on which a deduction may be required for its alkali blank.

After the combustion is complete, run the contents of the absorber into a 100-ml conical flask, and rinse the absorber, and the outlet wash tube from the combustion tube, 2–3 times with 3–5-ml portions of neutral distilled water. Add a known excess of 0.01 *N* sulphuric acid and a few drops of aqueous methyl red indicator, boil gently for 2–3 min, cool and then back-titrate with 0.01 *N* sodium hydroxide, after the addition of 8–10 drops of the screened indicator solution.

1 ml of 0.01 *N* NaOH = 0.3546 mg Cl or 0.7992 mg Br

B. Determination of chlorine (in presence of S and/or N)

Saturated mercuric oxycyanide solution

Shake 20 g of mercuric oxycyanide with 1 l of distilled water and set aside overnight. Filter this stock solution into a brown glass bottle and store away from strong light.

Procedure

Carry out the combustion, absorption and final titration with 0.01 *N* sodium hydroxide as described for *A*, but match the end-point of the titration against an equal volume of neutral distilled water and screened indicator solution contained in a second matched 100-ml conical flask. Add 10 ml of the stock mercuric oxycyanide

solution to the first flask and titrate the hydroxyl ions liberated with 0.01 *N* sulphuric acid until the colours of the two solutions again match. Add the same volume of 0.01 *N* sulphuric acid to the contents of the second flask together with 10 ml of mercuric oxycyanide solution and titrate with 0.01 *N* sodium chloride until its colour re-matches that of the first flask.

The chloride content of the original absorption solution ≡ volume of 0.01 *N* sodium chloride consumed, *i.e.*

1 ml of 0.01 *N* NaCl = 0.3546 mg Cl

C. Determination of bromine (in presence of S and/or N)

Method 1

Neutral mercuric oxycyanide solution. Carefully neutralise the stock solution with 0.01 *N* sulphuric acid in the presence of a few drops of methyl red/methylene blue screened indicator.

Procedure. Carry out the combustion, absorption and titration with 0.01 *N* sodium hydroxide as in *A*,*B*. Add to the neutralised absorption solution 10 ml of the neutral mercuric oxycyanide solution and titrate the released hydroxyl ions very carefully with 0.01 *N* sulphuric acid until a faint pink tinge is reached. A compensation titration is not necessary for bromide[9].

1 ml of 0.01 *N* H_2SO_4 = 0.7992 mg Br

Method 2 (based on method of Kolthoff and Yutzy[11])

Reagents (*a*) 5% Aqueous sodium hypochlorite solution: 90 ml of 14–15% bromine-free sodium hypochlorite solution diluted to 250 ml with distilled water.

(*b*) 50% Sodium formate solution: 32 ml of formic acid added slowly with cooling to 30 g of sodium hydroxide dissolved in a little water and finally diluted to 100 ml with distilled water.

(*c*) 5% Aqueous ammonium molybdate solution.

Procedure. In this case, the halogen is best absorbed in fairly strong alkali, hence it is advisable to reserve a separate absorber because alkali tends to adsorb on the glass surface and interferes with later acidimetric determinations.

Charge the bead-filled absorber with a mixture of 6–8 ml of 1 *N* sodium hydroxide solution and 5–6 drops of 35% bisulphite solution. Burn the sample as usual and transfer the resulting absorption solution, together with the aqueous washings from the absorber, to a 250-ml stoppered, conical flask; heat to boiling for a couple of minutes with 2–3 drops of 30% MAR hydrogen peroxide. Cool the contents of the flask quickly to room temperature and neutralise with 1 *N* phosphoric acid using aqueous methyl red as indicator. Add 5 ml of 5% hypochlorite solution, cover the flask with a watch glass and heat the solution slowly almost to boiling over a period of 8–10 min. Remove the flask from the source of heat, wash down its wall with a little distilled water and add 5 ml of 50% sodium formate solution. Mix the contents of the flask thoroughly by frequent swirling to ensure the complete destruction of the excess of hypochlorite solution. When the bromate solution has reached room temperature, add 5 ml of 9 *N* sulphuric acid, followed by 1–2 drops of 5% ammonium molybdate and *ca.* 0.5 g of solid potassium iodide. Stopper the flask, mix well and set aside for 5 min. Titrate the released iodine with 0.02 *N* sodium thiosulphate solution, adding a small quantity of Thyodene indicator just before the end-point is reached.

It is essential to carry out a blank determination on all the reagents, preferably by the combustion of a non-halogenated sample such as benzoic acid as a check on the absorption solution.

1 ml of 0.02 N $Na_2S_2O_3$ = 0.26639 mg Br

D. Determination of iodine (in the presence or absence of S and/or N)

Procedure

Charge the bead-filled absorber with 6–7 ml of 1 N sodium hydroxide and burn the sample as usual. Transfer the alkaline absorption solution to a 250-ml stoppered conical flask and wash the absorber thoroughly with water (3 × 3–5-ml portions). Neutralise the contents of the flask with 1 N phosphoric acid in the presence of a few drops of aqueous methyl red indicator solution. Then add 1.0–1.5 ml of saturated bromine water and allow the mixture to stand stoppered for 5 min. Destroy the excess of bromine by the dropwise addition of formic acid and test for complete removal of bromine with aqueous methyl red indicator. Add 5 ml of 2 N sulphuric acid and 0.5 g of solid potassium iodide and titrate the released iodine 2 min later with 0.02 N sodium thiosulphate in the usual way.

1 ml of 0.02 N $Na_2S_2O_3$ = 0.4231 mg I

ADDENDUM

Since the above work was completed, an interesting modification of the mercurimetric titration of chloride has been described by CHENG[16] who applied it after the oxygen flask method of decomposition of the organic material. The titration is done with 0.01 N mercuric nitrate solution in the presence of diphenylcarbazone indicator[17] but sufficient ethanol or isopropanol is added to give an approximately 80% alcoholic medium. This not only effects a startling improvement in the sharpness and clarity of the end-point but also achieves a more stoichiometric relationship.

The usual titration in aqueous media is unattractive on the microscale, for the end-point is indistinct. On any scale of working the titration is not stoichiometric and the reactions which occur appear to be complicated; probably a slight dissociation of the mercuric chloride complex, $HgCl_2$, is partly compensated by a tendency to form less stable mercury chloride complexes[18] such as $HgCl^+$. In any case it is advisable to standardise the titrant under the conditions of the actual determination.

CHENG used the method for bromine and chlorine determinations, taking sufficient sample to provide 1–1.5 mg of halogen, and standardised the titrant under the same conditions. We have found that a wider range is possible if the volume of solution used by CHENG is halved, *i.e.* if 10 ml of aqueous solution and 40 ml of ethanol are used. This procedure is suitable for 1–2 mg of halide, the titrant being standardised against an appropriate amount of alkali halide under similar conditions. Different 1-mg ranges can be used (up to 5 mg of chloride) so long as the titrant is standardised within the range taken. The method is not suitable for semimicro work.

This technique can profitably replace the mercuric oxycyanide method described above for all individual chlorine and bromine determinations; it is not suitable for iodine determinations or for mixed halogen determinations, hence the mercuric oxycyanide method is still retained for general purposes. Combustion and absorption are

carried out as described above in Procedure A. The inlet wash tube is rinsed with 1–2 ml of water and the absorber is detached and rinsed thoroughly with ethanol, 40 ml of which are added altogether. The solution is then neutralised with 0.05 *N* nitric acid and the determination completed as described by CHENG[16]. It is not necessary to remove hydrogen peroxide.

This procedure is also excellent after decomposition by the oxygen flask technique. Our present routine practice is to use the flask method except for highly volatile liquids or refractory compounds where the empty tube method has proved to give more reliable results.

ACKNOWLEDGEMENT

We are grateful to Professor R. BELCHER for his helpful advice and guidance in this work.

SUMMARY

A critical study has been carried out of titrimetric methods suitable for the microdetermination of each of the halogens, chlorine, bromine and iodine, in their possible organic combinations with the elements, oxygen, nitrogen and sulphur, following organic decomposition by the rapid empty tube combustion procedure.

RÉSUMÉ

Une étude critique a été effectuée sur les méthodes titrimétriques, utilisées pour le microdosage des halogènes (chlore, brome, iode) dans les substances organiques.

ZUSAMMENFASSUNG

Beschreibung einer kritischen Untersuchung über die Titrationsmethoden zur Mikrobestimmung von Chlor, Brom und Jod in organischen Substanzen.

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KINETICS OF DECOMPOSITION OF YTTRIUM, CEROUS AND ZIRCONYL OXALATES

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INTRODUCTION

Thermogravimetric and differential thermal analysis are used to study solid state decomposition reactions at high temperatures. The temperature of decomposition of some of the oxalates of lanthanides have been recently studied thermogravimetrically but the kinetics of decomposition has not been calculated. This paper reports the rate-dependent parameters of the decomposition of yttrium, cerous and zirconyl oxalates according to the methods of FREEMAN AND CARROLL[1], and BORCHARDT AND DANIELS[2].

EXPERIMENTAL

Yttrium oxalate and cerous oxalate were prepared from the respective nitrates (E. Mercks) by the method reported by WENDLANDT[3]. Zirconyl oxalate was prepared from its chloride (E. Mercks) according to TAKAGI[4].

A Stanton thermobalance (high temperature model) was used for the thermogravimetric measurements. The rate of heating was maintained at about 6°/min. Weight losses were within 2% of the theoretical values.

The apparatus for DTA was designed in this laboratory. Two platinum cells 8 mm in diameter and 15 mm high, with a capacity of 700 mg of tightly packed alumina, were used. The heating was controlled by a Honeywell-Brown programme controller-recorder, and the differential temperature was recorded by a differential mV recorder. The rate of heating was maintained at 5°/min.

For DTA study, the sample was well mixed with extra pure alumina (E. Merck's) and tightly packed in one cell whereas alumina alone as reference material was taken in the other.

RESULTS AND DISCUSSIONS

Yttrium oxalate

The analysis of the compound prepared for the present work corresponded to $Y_2(C_2O_4)_3 \cdot 9\,H_2O$. The thermogram (Fig. 1) showed that the water of hydration began to evolve at 60° and continued up to 200°. After this the curve became horizontal to the time and temperature axis with a constant weight region between 200°–260° corresponding to $Y_2(C_2O_4)_3 \cdot 2\,H_2O$. The dihydrate started decomposing at 260°. There was a break in the curve at 415°, the temperature at which the anhydrous $Y_2(C_2O_4)_3$ was obtained. Its decomposition into CO_2, CO and Y_2O_3 was complete at 640°.

In the DTA curve (Fig. 2), all the phases in the decomposition of $Y_2(C_2O_4)_3 \cdot 9\,H_2O$

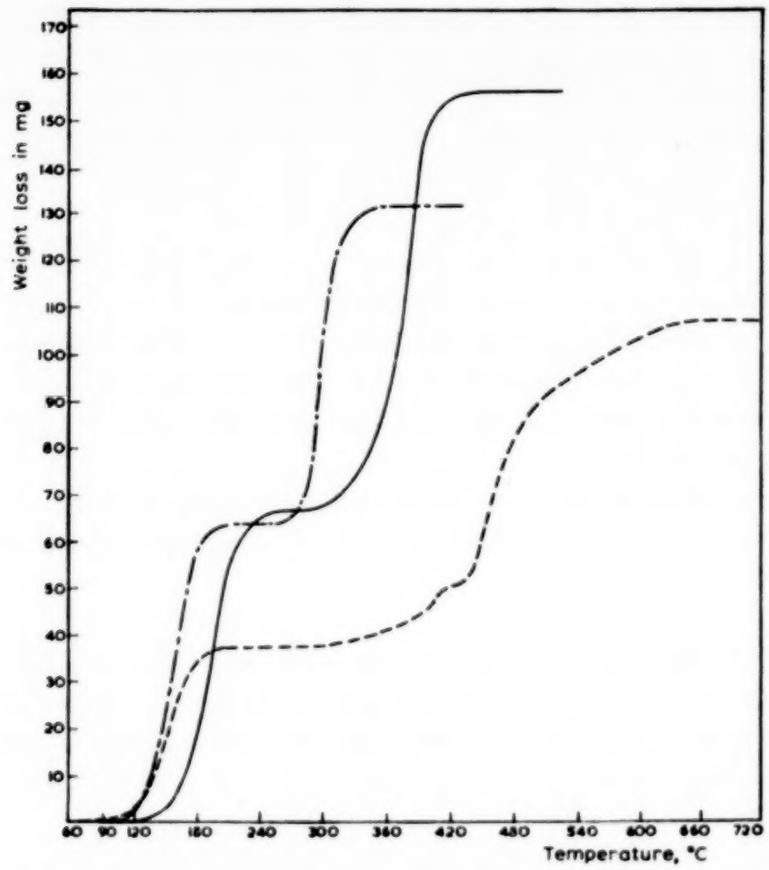

Fig. 1. Thermal decomposition of yttrium oxalate, cerous oxalate and zirconyl oxalate.
— — — yttrium oxalate; — · — · — · cerous oxalate; ———— zirconyl oxalate.

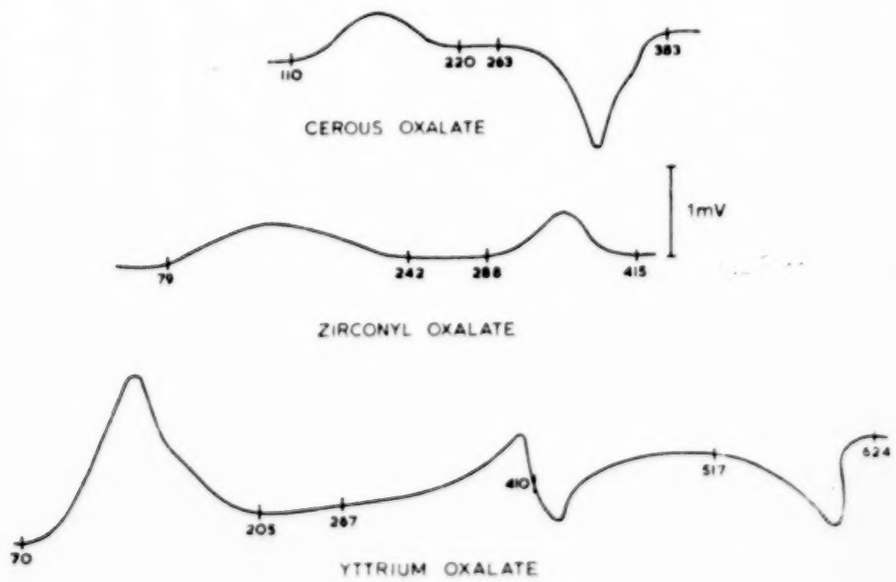

Fig. 2.

up to 410°, were similar to those in the thermogram but between 410° and 468°, a new phase appeared which was neither shown up in the above thermogram nor in that of WENDLANDT. This phase further decomposed giving Y_2O_3 at 624°.

A new sample of $Y_2(C_2O_4)_3 \cdot 9\ H_2O$ was very gradually heated in the DTA furnace

until a temperature of about $468 \pm 5°$ was reached. The furnace was then maintained at this temperature for about 30 min and the sample removed and air quenched. A portion of the product was then analysed. No oxalate was present. The estimation of CO_2 and Y_2O_3 in the sample showed that the formula of this intermediate product was $(YO)_2CO_3$.

Cerous oxalate

The compound prepared for this study corresponded to $Ce_2(C_2O_4)_3 \cdot 10\,H_2O$. The thermogram (Fig. 1) showed that it began to yield its water of hydration at 90°, and the anhydrous $Ce_2(C_2O_4)_3$ was obtained at 220°. The decomposition of the anhydrous compound commenced at 268° and was completed at 365°. The final end product on analysis was found to be CeO_2.

The data obtained here fully agree with that of WENDLANDT[3]. DTA studies also gave results (Fig. 2) identical to those obtained above from thermogravimetric analysis.

Zirconyl oxalate

The thermogram (Fig. 1) showed that the decomposition of $ZrO(C_2O_4) \cdot 3\,H_2O$ started at 85° and the dehydration was complete at 256°. The anhydrous oxalate decomposed rapidly from 285° and finally resulted in ZrO_2. Similar results were also obtained by DTA (Fig. 2).

CALCULATIONS OF RATE PARAMETER

To evaluate the kinetics of decomposition of the three oxalates by the thermogravimetric method, the following equation was used[1]:

$$\frac{-\frac{E^*}{2.3R}\,\Delta(T^{-1})}{\Delta \log Wr} = -x + \frac{\Delta \log (dw/dt)}{\Delta \log Wr} \qquad (1)$$

where E^* = energy of activation,
x = order of reaction,
T = absolute temperature,
t = time,
Wr = weight loss at completion of reaction minus weight loss up to time t,
dw/dt = rate of loss of weight with time,
R = gas constant.

$$\frac{\Delta \log (dw/dt)}{\Delta \log Wr} \; vs. \; \frac{\Delta(T^{-1})}{\Delta \log Wr}$$

was plotted for all the three metal oxalates. The order of reaction and the activation energy of dehydration and decomposition of the oxalates were calculated from the above curves.

The relation derived for the shape of DTA curves and the kinetics of the reaction in liquid by BORCHARDT AND DANIEL[2] has been found to apply to the studies of solids[5]. The relation for the first order reaction is given by

$$k = \frac{C_p\left(\frac{d\Delta T}{dt}\right) + K\Delta T}{K(A-a) - C_p\Delta T} \qquad (2)$$

where k = rate constant of reaction,
A = total DTA curve area,
C_p = total heat capacity of reactant solid or reference solid,
K = cell constant,
$\mathrm{d}\Delta T/\mathrm{d}t$ = shape of curve at time t,
ΔT = height at time t,
a = area at time t.

As quantities $C_p \cdot \dfrac{\mathrm{d}\Delta T}{\mathrm{d}t}$ and $C_p\,\Delta T$ are small, equation (2) could be reduced to

$$k = \frac{\Delta T}{A - a} \tag{2a}$$

The equation was extended to solids as the heat capacities of the reference material and the sample under study would not differ extensively if the packing of both cells were done the same way. From the plot of ln k *vs.* $1/T$, the activation energy E could be calculated from the equation

$$k = A' e^{-E/RT}$$

Typical plots for these equations are represented in Figs. 3 and 4, and the results summarized in Table I. It will be observed that there is good agreement between the values of decomposition temperatures obtained by DTA and thermogravimetry. Also since there is fairly good agreement found between the values of the activation energy

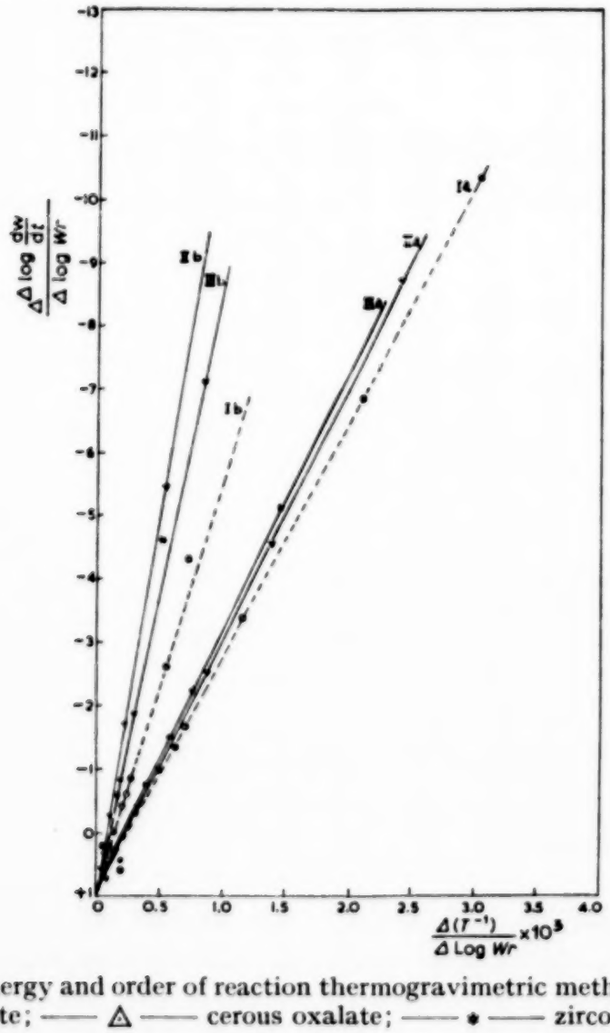

Fig. 3. Activation energy and order of reaction thermogravimetric method. — — ⊙ — — yttrium oxalate; —— △ —— cerous oxalate; —— • —— zirconyl oxalate.

obtained from these two data, the assumptions made by PADMANABHAN *et al.*[5] appear to be corroborated.

In the case of cerous oxalate, separate experiments were done to study its mode of

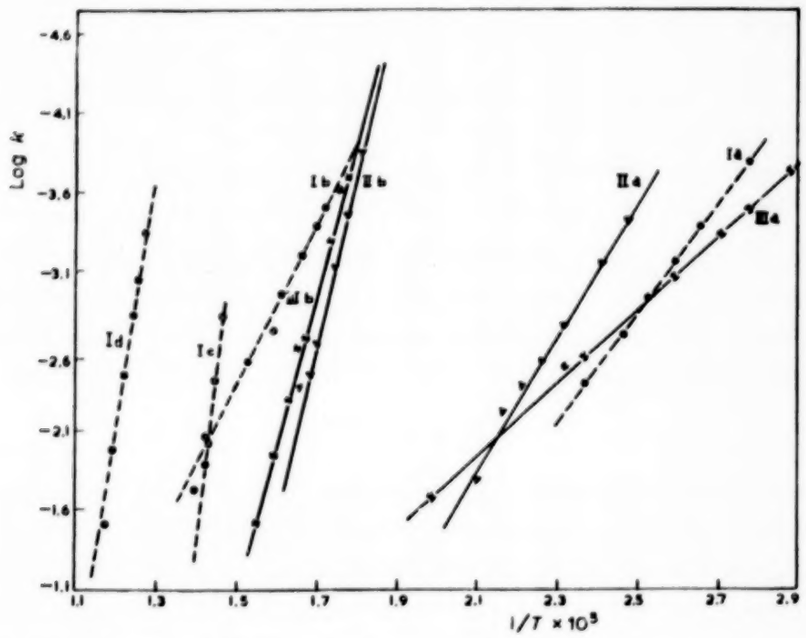

Fig. 4. Activation energy curve (DTA) —— ⊙ —— yttrium oxalate; —— △ —— cerous oxalate; —— * —— zirconyl oxalate.

TABLE I

DECOMPOSITION OF Y, Ce(III) AND ZrO OXALATES

	Temperature of decomposition		*Energy of activation*		*Order of reaction*
	TGA	*DTA*	*TGA*	*DTA*	
			in kcal/mol		
1. *Yttrium oxalate*					
$Y_2(C_2O_4)_3 \cdot 9\ H_2O \rightarrow Y_2(C_2O_4)_3 \cdot 2\ H_2O + 7\ H_2O$	60°	70°	17	17	0.85
$Y_2(C_2O_4)_3 \cdot 2\ H_2O \rightarrow Y_2(C_2O_4)_3 + 2\ H_2O$	260°	267°	30	24	0.90
$Y_2(C_2O_4)_3 \rightarrow (YO)_2CO_3 + 2\ CO_2 + 3\ CO$	415°[a]	410°	—	105	
$(YO)_2CO_3 \rightarrow Y_2O_3 + CO_2$	—	517°	—	78	
2. *Cerous oxalate*					
$Ce_2(C_2O_4)_3 \cdot 10\ H_2O \rightarrow Ce_2(C_2O_4)_3 + 10\ H_2O$	90°	110°	18.5	20	0.9
$Ce_2(C_2O_4)_3 \rightarrow Ce_2O_3 + 3\ CO + 3\ CO_2$ $Ce_2O_3 + O \rightarrow 2\ CeO_2$ $3\ CO + 3\ O \rightarrow 3\ CO_2$	268°	263°	56	51.5	1.0
3. *Zirconyl oxalate*					
$ZrO(C_2O_4) \cdot 3\ H_2O \rightarrow ZrO(C_2O_4) + 3\ H_2O$	85°	79°	18	11	0.85
$ZrO(C_2O_4) \rightarrow ZrO_2 + CO_2 + CO$	285°	288°	44	44.5	1.0

[a] Only a single step was observed.

decomposition. A weighed amount of the cerous oxalate was heated in the absence of air and the gases produced were analysed. The decomposition corresponded to

$$Ce_2(C_2O_4)_3 \rightarrow Ce_2O_3 + 3\ CO + 3\ CO_2$$

In the presence of air or oxygen, analysis of the gases showed that the decomposition corresponds to

$$Ce_2(C_2O_4)_3 + 2\ O_2 \rightarrow 2\ CeO_2 + 6\ CO_2$$

Since the DTA and the TGA were both done in air, the activation energies given in column 4 of Table I are for the overall reactions as shown in the first column.

ACKNOWLEDGEMENT

The authors wish to thank Dr. J. SHANKAR for helpful suggestions.

SUMMARY

The kinetics of the decomposition of yttrium, cerous and zirconyl oxalates have been studied thermogravimetrically and also by differential thermal analysis.

RÉSUMÉ

Les auteurs ont effectué une étude sur la décomposition des oxalates d'yttrium, de cérium(III) et zirconyle, par thermogravimétrie et par analyse thermique différentielle.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Kinetik der Zersetzung von Yttrium-, Cerium(III)- und Zirkonyloxalat mit Hilfe der Thermogravimetrie und durch differentialthermische Analyse.

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ANION EXCHANGE STUDIES OF ZIRCONIUM(IV) IN CITRATE SOLUTION

SEPARATION FROM MIXTURES

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Ion exchange studies of the important fission product elements[1] have been continued; zirconium(IV) has been investigated. Zirconium(IV) is known to form a strongly anionic citrate complex in 5% citric acid solution at pH *ca.* 2.7. TOMPKINS, KHYM *et al.*[2] used this for the elution of zirconium in presence of fission products such as cerium, barium and strontium. The cation exchange separation[3] of zirconium from titanium involved essentially the same principle; zirconium was completely eluted with 1% citric acid at pH *ca.* 1.75. The probable nature of the anionic citrate complex was found to be $[ZrO(HCit)_2]^{-2}$ at low pH, whereas $(ZrOCit)^-$ was predominant at higher pH.

KORKISCH AND FARAG[4] developed the anion exchange separation of zirconium from thorium, titanium, iron and aluminium by using the anionic sulphate complex of zirconium in 0.1 *N* sulphuric acid. Zirconium was then eluted with 4 *N* hydrochloric acid. This method was extended[4] for the determination of zirconium in silicate rocks. These workers have also studied the behaviour of the anionic ascorbate complex[4] of zirconium on an anion exchanger. The fluoride or oxalate complexes of zirconium[5] were used for its separation from hafnium on Dowex-1 resin, with 0.5 *N* hydrofluoric acid and 1 *N* hydrochloric acid as eluant. HUFFMANN *et al.*[6] used a similar principle for their separation with 0.2 *N* hydrochloric acid and 0.01 *N* hydrofluoric acid. The anionic chloride complex[7] of zirconium in 9 *N* hydrochloric acid formed the basis of the separation of zirconium from hafnium, niobium and tantalum. Zirconium has been separated from protoactinium[8] on Amberlite IRA-400 with 6–7 *N* hydrochloric acid as an eluant, and from aluminium[9] on Dowex-1 by means of its anionic complex in 0.06 *N* hydrochloric acid plus 0.8 *N* hydrofluoric acid.

However, no ion exchange studies of zirconium in citrate systems have been done so far. This paper describes such studies. The strongly basic quaternary ammonium type of anion exchanger Dowex 21K was utilised. Nitric acid, hydrochloric acid, perchloric acid and ammonium chloride were studied as the eluants. Zirconium was also separated from the important fission product elements *e.g.*, barium, strontium, caesium, cadmium, antimony, and also from lead and molybdate.

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APPARATUS AND REAGENTS

Apparatus

Ion-exchange column and Cambridge pH meter. The ion exchange column was identical to that previously described[1]; a resin bed 1.4 × 14.5 cm was utilised.

Reagents

Zirconium oxychloride stock solution, 5.24 mg per ml; 5.529 g of zirconium oxychloride (E. Merck & Co.) was dissolved in 300 ml of water containing about 2% hydrochloric acid. The solution was standardised gravimetrically as the oxide[10]. For ion exchange runs 36.68 mg of zirconium was taken.

Dowex 21K, (Dow Chemical Company, Midland, Mich. U.S.A.) 50–100 mesh, chloride-form anion exchange resin. This resin was conditioned as described earlier[1]. The resin was converted to the citrate form by washing with 50 ml of 5% citric acid solution and then with water till the effluent was free from citric acid. At the conclusion of the runs, the resin was withdrawn from the column, air-dried, dried in an oven at 100° for 1–2 h and weighed.

Chemicals used were all of reagent grade, unless otherwise mentioned.

EXPERIMENTAL, RESULTS AND DISCUSSION

Ion exchange behaviour studies

An aliquot of zirconium oxychloride solution containing 36.68 mg of zirconium was mixed with 25 ml of water in a 50-ml beaker. Solid citric acid was added to this, so that the solution was 5% with respect to citric acid and the pH was adjusted to 2.7–3.0 by means of 0.01 *N* ammonium hydroxide and 0.26 *M* citric acid solution with a pH meter. The solution containing the anionic citrate complex of zirconium was passed through the resin column at a rate of 1 ml per min. After adsorption the column was washed with 100 ml of water, and zirconium was then eluted with 300 ml of the various eluants at a rate of 2 ml per min. The eluting agents used were nitric acid (0.25, 0.50, 1.0 and 2.0 *N*); hydrochloric acid (0.50, 1.0, 2.0 and 4.0 *N*); perchloric acid (0.25 and 1.5 *N*) and ammonium chloride (1 *M*). The effluent batch (300 ml) was analysed for zirconium as the oxide after the destruction of citric acid by the usual nitric–perchloric acid treatment. Since citric acid complicates the analysis, the citrate complex must be decomposed and the liberated citric acid must be completely removed before the determination of zirconium. However, citric acid can be completely destroyed by two or three evaporations with nitric and perchloric acids.

The results (Table I) show that with 300 ml of nitric acid (0.25–2.0 *N*), or hydrochloric acid (0.50–2.0 *N*) as the eluting agent, essentially quantitative recovery of zirconium was possible. With perchloric acid or ammonium chloride as eluant, elution was incomplete. Hydrochloric acid (0.50–2.0 *N*) is suitable for routine work because of its volatility in the analysis step. Higher concentrations of hydrochloric acid[7] and sulphuric acid[4] itself were not used owing to their tendency to form the anionic complexes.

Ion exchange separations

Barium, strontium, lead, cadmium and caesium do not form anionic citrate complexes at pH 2.7–3.0, and can therefore be easily separated from zirconium by the

TABLE I

BEHAVIOUR OF THE ANIONIC CITRATE COMPLEX OF ZIRCONIUM(IV) TOWARDS VARIOUS ELUANTS

Zirconium = 36.68 mg; wt. of resin = 8.1476 g (oven dried)

No.	*Eluting agent*	*Eluant concentration M*	*Total zirconium recovery %*
1	HNO_3	0.25	96.3
	HNO_3	0.50	100.7
	HNO_3	1.0	97.3
	HNO_3	2.0	102.3
2	HCl	0.50	97.1
	HCl	1.0	102.1
	HCl	2.0	97.7
	HCl	4.0	104.7
3	$HClO_4$	0.25	7.3
	$HClO_4$	1.50	26.2
4	NH_4Cl	1.0	2.0

TABLE II

ION EXCHANGE SEPARATIONS

Zr = 36.68 mg

No.	*Foreign ion*		*Zirconium recovery %*
	added	*mg*	
1	Ba	72.8	100.9
2	Ba	36.4	100.1
3	Sr	72.0	102.5
4	Sr	36.0	101.5
5	Pb	71.4	101.4
6	Pb	35.7	99.8
7	Cs	71.7	101.7
8	Cs	35.9	102.0
9	Cd	72.0	102.9
10	Cd	36.0	103.2
11	Sb	9.0	113.4
12	U(VI)	71.4	135.1
13	Th(IV)	18.7	145.3
14	$Mo_7O_{24}^{-6}$	35.6	104.9

above method. The zirconium complex is retained in the bed while the cations pass through the column; the column is then washed with 100 ml of water, and zirconium is eluted with 300 ml of 2 *N* hydrochloric acid and determined as before.

Quantitative separations were obtained (Table II) except when antimony, thorium and uranium were present. The high results obtained in these cases were due to these elements being adsorbed under the same conditions as zirconium. It was observed that monovalent and divalent metals generally formed complexes at pH greater than 5.0 and did not interfere in the separation, whereas the trivalent and tetravalent elements formed complexes below pH 3.0 and so interfered. The method can be extended to

cover a large number of cations and can be used for the purification of zirconium from commonly associated cations.

Among anions, the separation of molybdate and vanadate from zirconium was examined. These ions were adsorbed along with zirconium. Zirconium was stripped with 300 ml of 1 *N* hydrochloric acid, the bed was then thoroughly washed acid-free with distilled water and finally molybdate and vanadate were eluted with 200 ml of 10% sodium carbonate. Molybdate did not interfere, but vanadate gave high results.

The separations of zirconium from barium, strontium, caesium, cadmium and molybdenum are significant since these metals are commonly associated as major fission product elements. Essentially similar separations can be achieved by using ethylenediaminetetraacetic acid (EDTA), but as EDTA causes complications in the effluent analysis, such studies were not undertaken.

The method can be adapted for large scale separations by using larger ion exchange columns. The total operations described in this work require 8–9 h. The results are reproducible to within $\pm 4\%$.

ACKNOWLEDGEMENT

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SUMMARY

The anion exchange behaviour of zirconium(IV) in a citrate system is described. Nitric acid, hydrochloric acid, perchloric acid and ammonium chloride were tested as eluants on Dowex 21K column. Zirconium is separated from fission product elements *e.g.*, barium, strontium, cadmium, caesium, molybdate and also from lead.

RÉSUMÉ

Les auteurs ont effectué une étude sur le comportement du zirconium, en vue de sa séparation sur échangeur d'anions d'avec les éléments de produit de fission, tels que Ba, Sr, Cd, Cs, Mo et Pb.

ZUSAMMENFASSUNG

Es wird gezeigt, dass Zirkonium von anderen Spaltprodukten wie Ba, Sr, Cd, Cs, Mo und Pb mit Hilfe von Ionenaustauschern getrennt werden kann.

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ION EXCHANGE RESINS IN STEEL ANALYSIS

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Ion exchange resins have been extensively used both in the analysis and study of many of the elements found in steels[1]. For example YOSHINO AND KOJIMA[2] separated iron and titanium on a cation exchanger; KAKIHANA[3] studied the behaviour of vanadium(V) on a polyfunctional sulphonated cation exchanger; FILIPPOVA[4] separated molybdenum and tungsten by adsorption on a cation exchanger, and selective elution with alkali; SUSSMAN[5] studied the behaviour of chromate solutions on anion exchangers; ALIMARIN AND MEDVEDEVA[6] separated the molybdenum, vanadium, and tungsten present in steel by using a cation exchanger and a sulphuric acid-hydrogen peroxide solution of the steel; and HAGUE[7] with an anion exchanger separated nickel, manganese, cobalt and iron by utilizing their ability to form chloro complexes.

However no systematic method has been described for the separation of chromium, vanadium and molybdenum from alloy steels by anion exchange resins and this paper describes such a separation of these metals before their quantitative estimation.

Iron is not normally estimated in steels, thus the ideal separation by ion exchange techniques would be the retention of all elements excepting iron. As the acidic character of an element increases with increasing valency it should be possible to separate vanadium(V), chromium(VI) and molybdenum(VI) from iron(III) and certain other elements by the use of an anion exchanger[5,6,8]. The adsorption of vanadium(V), chromium(VI) and molybdenum(VI) above pH 2.2, the isoelectric point of vanadium[2] does occur on an anion exchanger as indicated in the following experimental details.

However at pH 2.2 iron can precipitate from solution, but this precipitation of ferric ions can be overcome by forming stable complexes of iron with oxygen donors such as oxalic acid, citric acid, acetic acid and polyhydric alcohols[9], but with the exception of the monocarboxylic acid, acetic acid, increasing pH will aid the formation of anionic complexes. Thus at approximately pH 2.5 the iron(III)–mannitol complex is cationic yet sufficiently stable to prevent precipitation of the iron. The iron(III) acetate complex, whilst not as stable as the mannitol complex, is also cationic. A mixture of acetic acid, mannitol and ammonium hydroxide can then be used to adjust pH to approximately 2.5–3 with the iron still in solution as a cationic complex.

Phosphoric acid must be absent as it causes precipitation of a complex ferric phosphate[10] at about pH 2, and also keeps tungsten in solution. Tungsten (VI) is adsorbed by anion exchangers but its elution is unsatisfactory due to colloidal formation in

acid solution. The removal of tungsten is achieved by digesting the steel solution and filtering before adding to the resin column.

EXPERIMENTAL

A study of the behaviour of the elements concerned on the strongly basic anion exchanger DE-ACIDITE FF was first carried out. The elements were adsorbed on individual columns, containing approximately 25 ml of resin in the chloride form, from faintly alkaline 0.1 *M* vanadate, chromate, and molybdate solutions. 250 ml of the various eluting agents were passed down the column at controlled rates. Versenate is the sodium salt of ethylenediammine tetraacetic acid and sodium hydroxide was used throughout for pH adjustment.

A summary is given in Tables I–III of the results obtained. The actual elution values are dependent on such factors as weight of resin, volume of eluting agent and flow rates. However in the quantitative sense values of 0% and 100% only are of value.

The findings indicate that, relatively, vanadium(V) is only weakly adsorbed by the resin, that chromium(VI) is strongly adsorbed and in fact that reduction to chromium(III) is necessary for its elution, and that molybdenum(VI) is quite strongly adsorbed especially on forming complexes such as the chloro compound. This chloro complex formation of molybdenum is well illustrated in Table III.

TABLE I

ELUTION STUDIES ON VANADIUM(V)

Eluting agent	*Strength*	*% Elution*	*Remarks*
HCl	0–0.5 *N*	0–75	increasing elution with increasing acid strength
HCl	0.5–10 *N*	100	some reduction to vanadium(IV)
H_2SO_4	0–0.5 *N*	0–90	increasing elution with increasing acid strength
H_2SO_4	0.5–10 *N*	100	
H_3PO_4	0–1 *N*	0–50	increasing elution with increasing acid strength elution slow
H_3PO_4	2–8 *N*	50–100	elution slow
Oxalate	pH 2–11	0–100	increasing elution with increasing pH value
Versenate	pH 4–12	0–100	increasing elution with increasing pH value
Citrate	pH 2–12	0–100	increasing elution with increasing pH value
NaOH	0–0.5 *N*	0–100	quantitative elution at 0.5 *N*
NaOH	0.5–8 *N*	100	elution rapid beyond 2 *N*
NH_4OH	0.5–10 *N*	10–30	very slow qualitative elution

From the results given in Tables I–III, at least one separation technique has been shown possible, namely

(*a*) Elution of vanadium with 0.6 *N* sodium hydroxide.

(*b*) Elution of chromium with at least 4 *N* hydrochloric acid.

(*c*) Elution of molybdenum with 1 *N* hydrochloric acid.

TABLE II

ELUTION STUDIES ON CHROMIUM(VI)

Eluting agent	*Strength*	*% Elution*	*Remarks*
HCl	0–1 *N*	Nil	
HCl	4–10 *N*	100	Chromium reduced to trivalent state elution rapid beyond 6 *N*
H_2SO_4	0–1 *N*	Nil	
H_2SO_4	2–10 *N*	0–80	slow elution increasing with increasing acid strength Cr(III) formed
H_3PO_4	0–1 *N*	Nil	
H_3PO_4	2–8 *N*	0–10	very slight slow elution at 8 *N* acid strength
Oxalate	pH 2–12	trace	very slow qualitative elution at higher pH values
Versenate	pH 4–12	Nil	
Citrate	pH 2–12	0–10	very slow qualitative elution at higher pH values Cr(III) formed
NaOH	0–0.5 *N*	Nil	
NaOH	0.5–10 *N*	0–5	slow qualitative elution at higher strengths
NH_4OH	0.5–10 *N*	Nil	

TABLE III

ELUTION STUDIES ON MOLYBDENUM(VI)

Eluting agent	*Strength*	*% Elution*	*Remarks*
HCl	0–2 *N*	0–100	increasing elution with increasing acid strength
HCl	4–10 *N*	Nil	chloro complex strongly adsorbed
H_2SO_4	0–2 *N*	0–10	very slow qualitative elution
H_2SO_4	4–10 *N*	50–90	slow elution
H_3PO_4	0–1 *N*	Nil	
H_3PO_4	2–8 *N*	0–20	slow elution
Oxalate	pH 2–12	0–50	elution increasing with increasing pH values elution very slow
Versenate	pH 4–12	0–70	slow elution at higher pH values
Citrate	pH 2–12	0–50	slow elution increasing with increasing pH values
NaOH	0–0.8 *N*	Nil	
NaOH	1–10 *N*	0–100	increasing elution with increasing alkali concentration
NH_4OH	0.5–10 *N*	Nil	

Other separations may also be possible but this selected separation is rapid and does not involve the formation of very stable complexes which could interfere in the subsequent estimations.

Method of separation

A 0.5000-g sample of the alloy steel was dissolved in 20 ml of 4 *N* sulphuric acid. A few drops of nitric acid were then added and the solution digested for at least one hour. After filtering off the insoluble matter and precipitated tungsten, 5 ml 1 *N* silver nitrate solution were added to the filtrate followed by a few drops of 5% permanganate solution and some 2 g of ammonium persulphate. After developing the permanganate colour by boiling, 15 ml 1 *N* sodium chloride were added and the boiling continued to destroy the permanganate colour. On cooling, the solution was filtered if necessary, 1 g mannitol and 2 g ammonium acetate added and the volume adjusted to approximately 200 ml. The pH was then adjusted by dropwise additions of concentrated ammonium hydroxide to a value of 2.5–3. (The deep brown colour that develops serves as a useful guide to the volume of alkali required).

The solution was next added to the basic anion exchanger, DE-ACIDITE FF, approximately 25 ml of the resin having been lightly packed into a burette and converted to the nitrate form with sodium nitrate. The flow rate during adsorption and the subsequent water wash was of the order of 15 drops per min, and the total volume of solution and wash liquid was approximately 300 ml. The washing technique, as in the adsorption step, was downflow by inserting a flask fitted with a glass tube, cut angularly at the outlet end, into the top of the resin column.

Elution of the adsorbed vanadium, chromium and molybdenum was the next step. Some 200 ml 0.6 *N* sodium hydroxide was passed down the column at a flow rate of 5–10 drops per min followed by a water wash at the same flow-rate to give a final volume of 250 ml. This was then reserved for vanadium estimation. The chromium was eluted next with 200 ml 8 *N* hydrochloric acid at a flow rate of 5–10 drops per min and the washings made up to 250 ml with water. No water wash of the resin was used to avoid a premature elution of molybdenum. Finally the molybdenum was eluted with 200 ml 1 *N* hydrochloric acid at a flow rate of 5–10 drops per min, and the volume adjusted to 250 ml.

Estimation of the separated metals

Vanadium was estimated spectrophotometrically by the hydrogen peroxide method using 50-ml aliquots[11,12].

Chromium was estimated spectrophotometrically using the diphenylcarbazide method[11,12]. The 5-ml aliquot of chromium solution was first oxidised to the hexavalent state with bromine in alkaline solution and the excess bromine removed with phenol.

Molybdenum was estimated on a 25-ml aliquot by the thiocyanate colorimetric method[11,12].

TABLE IV

Element	*No. 1*	*No. 2*	*No. 3*
Vanadium	0.82%	1.02%	0.30%
Chromium	3.32%	4.08%	2.50%
Molybdenum	0.55%	0.40%	0.50%
Tungsten	16.12%	18.05%	10.02%
Nickel	0.43%	0.09%	2.84%
Cobalt	4.35%	0.11%	Nil
Manganese	0.22%	0.33%	0.30%

RESULTS

The certified steels chosen for the analyses had a composition as mentioned in Table IV; the results of seven separate analyses on each steel are as given in Table V.

TABLE V

Elemen	*Sample No.*	*Mean % found*	*Present %*
Vanadium	1	0.79	0.82
Vanadium	2	0.97	1.02
Vanadium	3	0.29	0.30
Chromium	1	3.28	3.32
Chromium	2	4.00	4.08
Chromium	3	2.47	2.50
Molybdenum	1	0.52	0.55
Molybdenum	2	0.38	0.40
Molybdenum	3	0.48	0.50

Probable errors are: Vanadium $\pm 0.02\%$, Chromium $\pm 0.05\%$ and Molybdenum $\pm 0.02\%$.

These results compare favourably with those obtained using other separation techniques, such as the mercury cathode deposition, whilst the method can be readily adapted to the simultaneous analysis of many steel samples. The time for one or more analyses is approximately 6 h.

SUMMARY

The metals vanadium, chromium and molybdenum may be separated from the other constituents of steel by passing an acetate buffered solution of the steel through a strongly basic anion exchanger and selectively eluting the above metals from the resin column with aqueous solutions of 0.6 *N* sodium hydroxide, 8 *N* hydrochloric acid and 1 *N* hydrochloric acid, respectively.

RÉSUMÉ

Une méthode est proposée pour la séparation du vanadium, du chrome et du molybdène d'avec les autres constituants d'un acier, en utilisant des résines d'échange d'ions.

ZUSAMMENFASSUNG

Beschreibung eines Verfahrens zur Abtrennung von Vanadium, Chrom und Molybdän von anderen Metallen in Stahl mit Hilfe von Ionenaustauschern.

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USE OF CARBOXYLIC ACID CATION EXCHANGE RESIN IN THE ANALYSIS OF COPPER IN CHROMATED WOOD PRESERVATIVE SOLUTIONS

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INTRODUCTION

Mixtures of copper sulphate–sodium dichromate, copper sulphate–zinc sulphate–sodium dichromate, copper sulphate–sodium arsenate–sodium dichromate and copper sulphate–borax–sodium dichromate are widely used as wood preservatives. The method usually employed for the analysis of copper in these solutions involves the removal of dichromate by a series of rather lengthy analytical operations[1]. The successful application of cation exchange resins (sulphonic acid resins) to isolating copper from water[2,3] and milk[4] prior to its estimation, indicated that an improved method for separating copper from dichromate could be developed by a similar approach. This paper describes the use of carboxylic acid resins for this purpose. Because of the high selectivity of these resins for copper[5], together with their ease of regeneration[6], only small sized resin columns are required. This will reduce the time required for the separation. Carboxylic acid resins, unlike sulphonic acid resins, have received little attention in analytical chemistry.

EXPERIMENTAL

Pretreatment of ion exchange resin

Fines were removed from 20–30 g Amberlite IRC-50 0.3–0.5 mm resin by repeatedly washing the resin with water, allowing the larger particles to settle and decanting off the fines. The resin was slurried into a 20 cm long, 2 cm internal diameter ion exchange column of conventional design.

Absorbed metals were removed from the resin by washing it with 200 ml 2 *N* HCl. □ The resin was washed with 250 ml deionised water before being converted into the ammonium form by treatment with 200 ml 2 *N* NH_4OH and 200 ml 2 *N* NH_4Cl at a flow rate of 0.25 ml/min.

The resin was finally washed with 200 ml deionised water, removed from the column, air dried and stored in a polythene bottle.

Preparation of ion exchange column

A 5-cm long resin bed was prepared in a 22-cm long pyrex tube having an inside diameter of 1 cm and fitted with a ground-glass tap at the lower end. The resin bed was supported on a glass wool plug. Under the working conditions employed below, a column of the above dimensions had a break-through capacity of 1.4 mequiv. Cu^{+2}.

PROCEDURE

An aliquot of wood preservative solution containing 0.2–0.6 mequiv. Cu^{+2} was pipetted into a small beaker and 5 *N* NH_4OH was added dropwise until the precipitate of basic copper salt had dissolved. An additional 2–3 drops of NH_4OH solution was then added. The resultant solution was transferred to the column head and soaked into the resin at a flow rate of 0.25 ml/min. 10 ml deionised water was used to complete the transfer of the sample to the column. A blue band of absorbed copper ions was clearly visible at the top of the resin bed at this stage. When the liquid level in the column head had almost reached the top of the resin bed, the resin was washed with 20 ml deionised water at a flow rate of 0.25 ml/min. The effluent, which contained the anions present in the preservative solution, was discarded. When the liquid level in the column had almost reached the top of the resin bed, the absorbed copper was eluted with 20 ml 2 *N* HCl at a flow rate of 0.25 ml/min. The HCl effluent was collected in a 150-ml beaker. After adjusting the pH of the hydrochloric acid effluent to 4.0–4.5 with ammonium hydroxide and acetic acid, the copper was estimated volumetrically with standard thiosulphate solution. On completion of the elution step the resin was transferred to a used resin container. When sufficient resin had accumulated, it was treated from □ under *Pretreatment of ion exchange resin.*

RESULTS

Known amounts of a synthetic copper sulphate–sodium dichromate solution (0.47 g $CuSO_4 \cdot 5\ H_2O$ and 0.75 g $Na_2Cr_2O_7$/100 ml) were analysed by the procedure described above. The results are listed in Table I.

A number of commercial chromated wood preservative solutions were also analysed. The results are given in Table II.

TABLE I

Cu present (mg)	*Cu found (mg)*	*Recovery (%)*
6.0	6.0	100.0 (99.2)
	5.9	98.3
12.0	12.0	100.0 (100.0)
	12.0	100.0
24.0	23.9	99.5 (99.8)
	24.0	100.0

TABLE II

Preservative	*Cu present in 10 ml aliquot (mg)*[a]	*Cu found by present procedure (mg)*	*Recovery (%)*
Chromated copper sulphate	5.1	5.1	100.0 (100.0)
		5.1	100.0
Chromated copper arsenate	10.0	10.1	101.0 (100.0)
		9.9	99.0
Chromated copper sulphate–Borax	15.3	15.2	99.3 (99.7)
		15.3	100.0

[a] Determined gravimetrically with cupron[7].

DISCUSSION

The cation exchanger was converted to the ammonium form before use for the following reasons. Exchange rates are higher when the resin is in the salt form[6]. If the resin was in the hydrogen form, the hydrogen ions liberated by the uptake of the Cu^{+2} ions may upset the pH of the influent solution and cause incomplete uptake of the Cu^{+2} ions. Cations are not taken up appreciably by carboxylic acid resins[6] in solutions below pH 7.

The time taken for the proposed method was approximately half-an-hour. Because of its simplicity, the present method lends itself to multiple routine analysis. For this purpose a number of columns can be arranged in series so that one column is available per sample.

ACKNOWLEDGEMENTS

The above work was carried out in the Government Chemical Laboratories, Cape Town. The author wishes to thank the Department of Agricultural Technical Services for the facilities provided.

SUMMARY

An ion exchange separation, using carboxylic acid resin, combined with a thiosulphate titration is suggested as a rapid and accurate method for the determination of copper in chromated wood preservatives.

RÉSUMÉ

Une méthode est proposée pour le dosage du cuivre dans des solutions destinées au traitement du bois (séparation par une résine d'échange d'ions et titrage par le thiosulfate).

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Kupfer in Holzimprägnierungsmittel durch Titration mit Thiosulfat nach vorheriger Trennung von Chromat mit Hilfe eines Jonenaustauschers.

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THE APPLICATION OF CHELATE SYSTEMS TO PARTITION CHROMATOGRAPHY: PRELIMINARY PAPER

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INTRODUCTION

A considerable amount of effort has been devoted in the past to the development of techniques which may be used for the separation of metals, and of these, two methods, solvent extraction and chromatography, have been very widely applied.

In both cases, the distribution of a metal, in one or more forms, between two phases, is involved, but whereas solvent extraction most frequently utilizes an immiscible liquid-liquid solvent pair, in chromatography other than gas chromatography the phases are either a liquid and a solid, or else two liquids, one of which is rendered immobile by retention on a solid. The selectivity of this type of process can usually be considerably improved by careful control of acidity, and the addition of competitive complexing agents to one or both phases.

Solvent extraction has gained much favour by virtue of the very wide range of organic and inorganic ligands available that can be used in combination to afford the satisfactory separation of many metals. However, if the separation factor for two metals is not large even under optimum conditions, it will be necessary to repeat the extraction a number of times. If a batch extraction technique is used it is likely to prove both time consuming and tedious.

In order to overcome this difficulty, continuous[1] and continuous countercurrent[2] methods have been devised in which one or both of the phases involved in the extraction process are continuously replaced, whilst discontinuous countercurrent equipment[3] will allow a large number of batch extractions to be carried out in sequence with comparative ease.

The nature of the species involved in the distribution of a metal between a chromatographic column and a solvent cannot be as widely varied as between two solvents, but since a solute passing through a column undergoes a series of successive equilibrations, even small separation factors are of value. It would clearly be an advantage if the complexing agents, familiar in liquid–liquid extractions could be used in the form of a column, and this has been done already for 8-hydroxyquinoline[4], 8-hydroxyquinoline, β-naphthoquinoline and cupferron, either alone or mixed with potato starch[5] and dimethyl glyoxime, either alone or mixed with calcium carbonate or magnesium carbonate[6].

Direct interaction of this kind between a metal in aqueous solution and the solid complexing agent is likely to occur extremely slowly if one of the very hydrophobic

ligands is used, and a wetting agent must be added to the aqueous phase to achieve a reasonable reaction rate. This complication has been avoided by CARRITT[7] who made up columns of cellulose acetate coated with dithizone which he "wetted" with a small amount of carbon tetrachloride before passing the aqueous solution through them. These columns have proved rather unstable, but there would appear to be advantages in a reverse phase partition technique of this type in which the organic phase is held stationary since it requires the minimum pretreatment of the metal solution.

For satisfactory operation the solvent must adhere firmly to the support material, also both the complexing agent and the metal complex should have large partition coefficients in favour of the organic phase, if they are not to be eluted off the column in appreciable quantities.

It has been found that these requirements are fulfilled by solutions of certain chelating agents on silica gel and in this paper preliminary work is reported which has been carried out to determine the behaviour of dithizone in such a system. Since the inception of this work a reverse phase partition method for the separation of uranium has been reported[8].

THEORETICAL CONSIDERATIONS

The reaction between an n-valent metal M^{+n} and dithizone, here represented as a monobasic acid HL, in the aqueous phase of a two phase system is conventionally represented by

$$M^{+n} + nHL \rightleftharpoons ML_n + nH^+$$

with an equilibrium constant for the reaction K where

$$K = \frac{[ML_n][H^+]^n}{[M^{+n}][HL]^n} \tag{1}$$

square brackets denoting concentrations, which are used in place of activities for solutions of constant ionic strength. The chelate and reagent are assumed to partition into an organic phase with partition coefficients P_c and P_r such that

$$P_c = \frac{[ML_n]_0}{[ML_n]} \tag{2a}$$

$$P_r = \frac{[HL]_0}{[HL]} \tag{2b}$$

the subscript '0' distinguishing the species in the non-aqueous phase. Provided that all the equilibria in the system are accounted for by equations (1), (2a), (2b), it has been shown by numerous authors[9] that

$$\frac{[ML_n]_0}{[M^{+n}]} = \frac{KP_c}{P_r^n} \cdot \frac{[HL]^n_0}{[H^+]^n} = \frac{K'[HL]^n_0}{[H^+]^n} \tag{3}$$

The fraction extracted is defined by

$$E = \frac{\Sigma[M]_0}{\Sigma[M]}$$

In the simplest case, where P_c is large and it is possible to neglect lower dithizone

complexes, ML, ML_2 . . . ML_{n-1}, and other complexes MX, MX_2 . . . MX_j (which may be cationic or anionic), $[ML_n]_0/[M^{+n}]$ may be identified with the fraction extracted. If an anion X^- is present in the aqueous phase, which is capable of forming the non-extractable species $MX^{+(n-1)} + \ldots + MX_n$ with the metal M^{+n}, then

$$\Sigma[M]_W = [M^{+n}] + [MX^{+(n-1)}] + \ldots\ldots + [MX_n]$$
$$= [M^{+n}]\{1 + K_1[X^-] + K_1K_2[X^-]^2 \ldots K_1K_2 \ldots K_n[X^-]^n\} \quad (4)$$

the formation constant K_j being defined by

$$K_j = \frac{\left[MX_j^{+(n-j)}\right]}{\left[MX_{j-1}^{+(n-j+1)}\right][X^-]}$$

So equation (3) now becomes

$$E = \frac{K'[HL]_0^n}{[H^+]^n}\{1 + K_1[X^-] + K_1K_2[X^-]^2 + \ldots + K_1K_2 \ldots K_n[X^-]^n\} \quad (5)$$

It is frequently the practice in extraction experiments to maintain $[X^-]$ constant when equation (5) may be rewritten in a form similar to that of equation (3)

$$E = K'' \frac{[HL]_0^n}{[H^+]^n} \quad (3b)$$

but now the constant refers to a particular X^- concentration in the aqueous phase.

Equation (5) could still account for the behaviour of a solution of chelating agent held on silica gel, during the extraction of a metal, if the only function of the support was to act as inert diluent. This would also be true if the non-aqueous solution was retained on the surface of the silica, but in the latter case the concentration per unit weight would vary with particle size.

Alternatively the behaviour of the dithizone-containing support may be considered to be closely analogous to that of an ion exchange resin in that it consists of an immobilised organic substrate, capable of exchanging its protons for metal ions present in the aqueous phase.

The immediate objects of the present work were to investigate the distribution of a metal between an aqueous phase and a solution of a chelating agent retained on silica gel, and by means of equation (5) to ascertain if the extraction process was similar to that involved in the corresponding liquid–liquid extraction.

EXPERIMENTAL

Silica gel was precipitated from sodium silicate solution with 10 *N* hydrochloric acid in the manner suggested for partition chromatography[10], dried and graded, the fraction 85–120 mesh being retained.

Purification of the gel for use in the copper-dithizone system was carried out by allowing it to stand under successive volumes of concentrated hydrochloric acid until the supernatant acid remained colourless[11], then, after washing with water, it was shaken with a strong ethylenediamine-tetraacetic acid solution at a pH of approxi-

mately 5. Finally, after again being washed with water, alcohol and ether, the gel was dried at 110°.

Silica gel, prepared in this way, was placed in a beaker and just covered with a strong solution of dithizone, which had previously been purified[12]. The organic solvent was then evaporated off until a freely running powder was obtained, which was stored in a desiccator over the organic solvent, in the dark. The dithizone content of the samples of treated silica gel, used in these experiments, was found to lie between 10^{-6} and 10^{-5} mol of dithizone per g of support, but this could be considerably increased if required.

Before being used the silica gel was removed from this desiccator, and exposed to the air for 40 min to allow time for surplus organic solvent to evaporate and the gel to achieve constant weight.

20 ml of an aqueous hydrochloric acid phase and a weighed amount of silica gel (~0.1 g) containing dithizone were placed in a 50-ml flask and a small amount ($\sim 1 \cdot 10^{-8}$ mol) of radioactive copper (^{64}Cu) added in hydrochloric acid solution. For liquid–liquid extractions the solid phase was replaced by 20 ml of a solution of dithizone in either chloroform or carbon tetrachloride.

The flask and its contents were then very gently shaken mechanically for half an hour on a wrist action shaker, a time longer than that found necessary for the system to come to equilibrium.

Only when both the acidity of the aqueous phase was high and the organic solvent was carbon tetrachloride, did the dithizone solution show any tendency to strip off the support.

Solid–liquid extractions were duplicated with samples of silica gel treated with organic solvent, but no dithizone, and these experiments showed that in the absence of chelating agent, no extraction occurred. It would therefore appear that removal of copper from the aqueous phase was effected by chelation only, and not by adsorption. Liquid phases were always presaturated with the other solvent present in the system.

After equilibration the contents of the flask were either filtered through a glass sinter, which did not adsorb any copper at the acidities used, or centrifuged, and the activity and acidity of the aqueous phase determined. The activity was compared with that of a standard made up of 20 ml of the hydrochloric acid solution, and an amount of radioactive copper equal to that used in the extraction. Correction was made for the decay of 12.8 h copper.

The dithizone content of the silica gel was obtained as follows. A weighed amount of silica gel was treated with quantities of ammonia solution until all the dithizone was in aqueous solution. The combined aqueous extracts were made acid and the precipitated dithizone dissolved in a known volume of carbon tetrachloride. The optical density of this solution was measured, and using a value of $34.6 \cdot 10^3$ for the extinction coefficient of dithizone in carbon tetrachloride[13] the dithizone content of the original sample calculated.

DISCUSSION

The plot of log *E versus* the acidity of the aqueous phase is given in Fig. 1 for the case where the organic solvent on the silica gel was carbon tetrachloride (line A), and this is compared with a similar plot for the distribution of copper between an aqueous

hydrochloric acid phase and a dithizone–carbon tetrachloride phase (line B). Equivalent experiments with chloroform as the organic solvent gave the results plotted in Fig. 2.

If the species involved in the liquid–liquid and liquid–solid extractions are the same, then from equation (5)

$$\frac{E_A}{E_B} = \frac{K'_A}{K'_B} \frac{([HL]_0)^n_A A}{([HL]_0)^n_B B} \frac{[H^+]^n_B B}{[H^+]^n_A A} \frac{\{1 + K_1[X^-]_B + K_1K_2[X^-]^2_B + \ldots + K_1K_2 \ldots K_n[X^-]^n_B\}}{\{1 + K_1[X^-]_A + K_1K_2[X^-]^2_A + \ldots + K_1K_2 \ldots K_n[X^-]^n_A\}} \quad (6)$$

where subscripts A and B refer to the liquid–solid and liquid–liquid systems respectively. If $[HL]_0$ is virtually unchanged by extraction, equation (6) reduces to

$$\frac{E_A}{E_B} = K_{[HL]} \frac{[H^+]^n_B B \{1 + K_1[X^-]_B + K_1K_2[X^-]^2_B + \ldots + K_1K_2 \ldots K_n[X^-]^n_B\}}{[H^+]^n_A A \{1 + K_1[X^-]_A + K_1K_2[X^-]^2_A + \ldots + K_1K_2 \ldots K_n[X^-]^n_A\}} \quad (7)$$

and for the same hydrochloric acid concentration if $n_A = n_B$

$$\text{Log } E_A - \text{log } E_B = \text{constant} \quad (8)$$

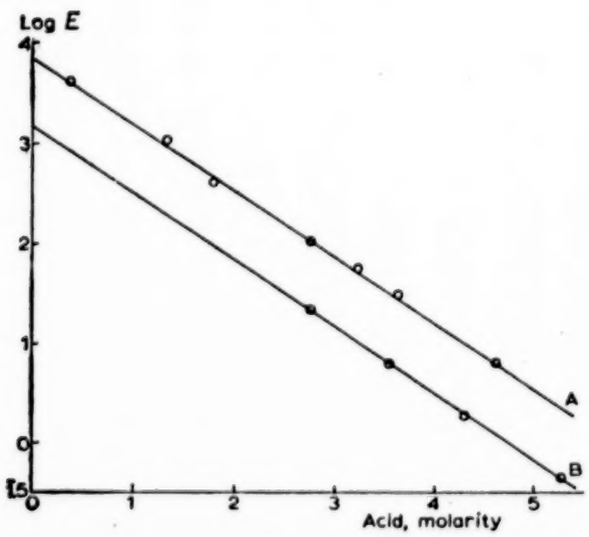

Fig. 1. The extraction of copper from an aqueous hydrochloric acid phase into a solution of dithizone in carbon tetrachloride. For curve A the solution was retained on silica gel. Dithizone concentrations, for curve A $2.4 \cdot 10^{-3}$ m/kg, for curve B $2.37 \cdot 10^{-4}$ m/l.

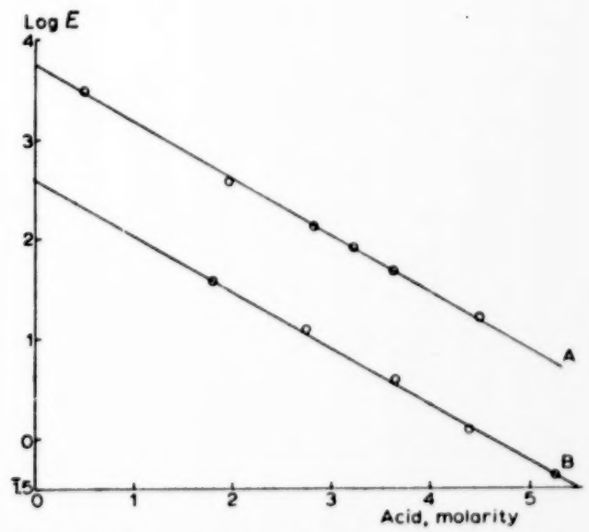

Fig. 2. The extraction of copper from an aqueous hydrochloric acid phase into a solution of dithizone in chloroform. For curve A the solution was retained on silica gel. Dithizone concentrations for curve A $7.9 \cdot 10^{-3}$ m/kg, for curve B $6.0 \cdot 10^{-4}$ m/l.

Since curves A and B, Figs. 1 and 2, satisfy equation (8), and by comparison with the liquid–liquid system, it would appear that $n_A = n_B = 2$, implying that two protons are liberated during the formation of a complex between copper and dithizone retained on silica gel. The vertical separation of lines A and B will give a measure of

$$\frac{K'_A}{K'_B} \frac{([HL]_0)^n_A A}{([HL]_0)^n_B B}$$

and consequently if $([HL]_0)^n_A A$ and $([HL]_0)_B B$ are known K'_A/K'_B may be found. This

has not been calculated because of the lack of any accurate information as to the nature of the dithizone species on the silica gel.

The similarity in the extraction behaviour of the liquid–solid to the liquid–liquid system, suggests that the same control of the acidity of the aqueous phase, which is of such value for regulating the partition of the metal between the two phases of the solvent extraction system, may be equally well used to vary the fraction of metal extracted, when the chelating agent is retained on silica gel, and if this closeness in behaviour is maintained for the extraction of other metal dithizonates it should be possible to adapt many of the liquid–liquid separations to work on the column principle. Qualitative experiments, to be reported at a later date, have also shown that metals, held by a dithizone column of this type, may be eluted by aqueous solutions of complexing agents.

It would, therefore, seem that columns containing solutions of chelating agents have considerable potentialities for separating metals, since a normal chromatographic separation may be enhanced by the addition of sequestering reagents to the aqueous phase, and the careful control of acidity, to provide selective extraction or elution.

ACKNOWLEDGEMENTS

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SUMMARY

It has been found possible to retain solutions of chelating agents on a solid supporting medium, and in this paper preliminary investigations are reported which were carried out to determine the extraction behaviour of radioactive copper between an aqueous hydrochloric acid phase and a solution of dithizone in an organic solvent retained on silica gel. Chloroform was found to be a very satisfactory solvent and carbon tetrachloride was also used. For both of these solvents the extraction *vs.* acidity curves were found to be similar to the corresponding liquid–liquid extraction. The high values for the fraction extracted show that this method would provide a useful technique for the concentration of copper from aqueous solution, and the similarity between the liquid–liquid and liquid–solid extractions suggests that it may be possible to adapt conventional liquid–liquid extractions to work on the column principle.

RÉSUMÉ

Une étude préliminaire a été effectuée sur l'application des chélates à la chromatographie de partage. L'auteur a examiné le comportement d'un cuivre radioactif entre une phase aqueuse–acide chlorhydrique et une solution de dithizone dans un solvant organique, sur silicagel.

ZUSAMMENFASSUNG

Es wurde gefunden, dass chelatbildende Reagenzien von festem Trägermaterial, wie Silicagel, aufgenommen werden können. Es wurde das Verhalten von radioaktivem Kupfer in salzsaurer Lösung bei der Extraktion mit einem Dithizon enthaltenden organischen Lösungsmittel in Gegenwart von Silicagel untersucht. Auf die Möglichkeit der Anreicherung von Metallen durch Extraktion unter Zuhilfenahme von Kolonnen wird hingewiesen.

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COLORIMETRIC DETERMINATION OF URANIUM(VI)

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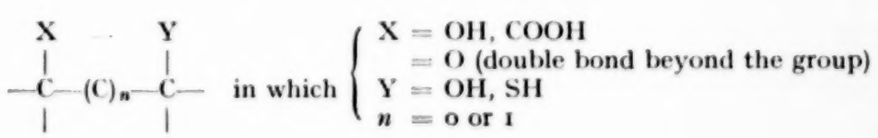
Derivatives of salicylic acid have occasionally been used as reagents for the colorimetric determination of uranium(VI). Salicylic acid itself was employed by MÜLLER[1].

A study[2] of organic reagents for the identification and colorimetric determination of uranium(VI) has shown that this element reacts preferentially with organic reagents which contain the following general atomic grouping:

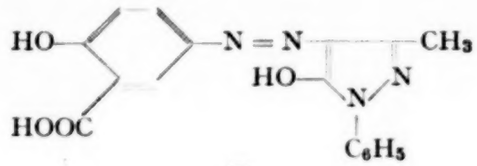


It was suggested that this group was the active functional group for uranium(VI). Three new reagents for uranium(VI) which possess this functional group were proposed, namely: the sodium salt of *p*-aminosalicylic acid, the sodium salt of *p*-nitrobenzene-azosalicylic acid (Alizarin Yellow R) and the sodium salt of *m*-nitro-benzene-azosalicylic acid (Alizarin Yellow G.G.). These reagents permit the colorimetric determination of uranium(VI) in the respective ranges 34.5–414 μg/ml, 6.9–69 μg/ml, and 6.9–82.8 μg/ml. Benzene-azosalicylic acid and Alizarin Yellow RS have also been proposed for the colorimetric determination of uranium[2], the respective ranges being 6.9–41.4 μg/ml and 6.9–55.2 μg/ml.

Recently, the ammonium salt of 4,4′-bis-[(azo-5)-salicylic] acid was proposed for the colorimetric determination of uranium[3].

In the present paper is described the colorimetric determination of uranium by means of a reagent which contains the above group and also an heterocyclic ring. This reagent was chosen because its diverse substituents favourably influence the sen-

sitivity of the reaction with uranium. The reagent is 1-phenyl-3-methyl-4-(3′-carboxy-4′-hydroxyphenyl-azo)-pyrazol-5-one (I).



(I)

REAGENTS AND PROCEDURE

Reagent

A solution of $UO_2(NO_3)_2 \cdot 6H_2O$ in water, containing 138 μg U/ml. The reagent was used as a 0.2% solution in ethyl alcohol.

Experimental

To a 10-ml graduated flask were added a volume varying up to 3 ml of the uranium nitrate solution and 1 ml of the reagent solution, and the mixture was diluted to the mark with ethanol. A comparison solution was prepared containing the same quantity of reagent as the test solution. Readings were made with a M53 filter on a Pulfrich vertical spectrophotometer (Russian model). Filters M43, M47 and M50 were not suitable for the extinction measurements. The pH of the solutions was always adjusted to a value of 5–6. The results of the determinations are shown in Tables I

TABLE I

μg U/10 ml	496 mμ	533 mμ	574 mμ	619 mμ	665 mμ
276	unreadable	0.65	0.12	0.04	0.00

TABLE II

ml of solution $UO_2(NO_3)_2 \cdot 6\,H_2O$	μg U(VI)/10 ml	M53 Extinction
0.125	17.25	0.035
0.25	34.50	0.08
0.5	69	0.16
1.0	138	0.32
2.0	276	0.65
3.0	414	0.93

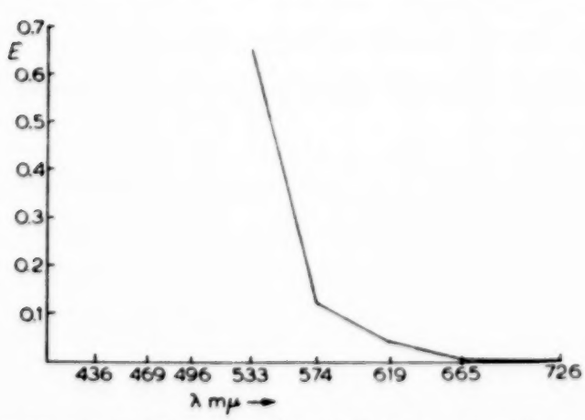


Fig. 1. The absorption spectra of the complex UO_2^{+2}–reagent I. c = 276 μg U(VI)/10 ml.

and II; the absorption spectrum and extinction curves are recorded in Figs. 1 and 2.

The results given indicate that the proposed method is suitable for the colorimetric determination of uranium(VI) in the range 1.72–41.4 μg/ml; the method is therefore one of the most sensitive for this element.

The influence of pH on the extinction has been studied, the results being recorded in Fig. 3.

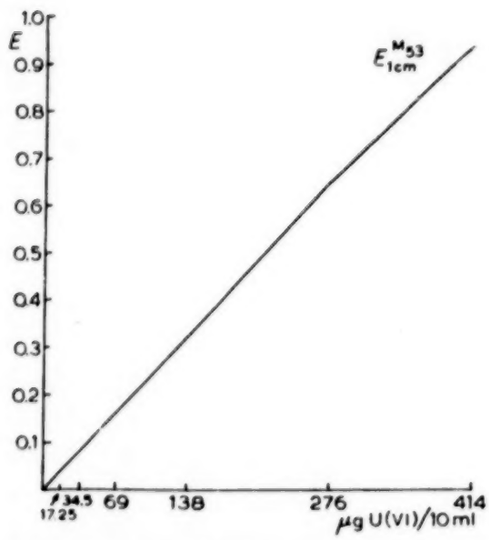


Fig. 2. The extinction curve of the complex UO_2^{+2}–reagent I.

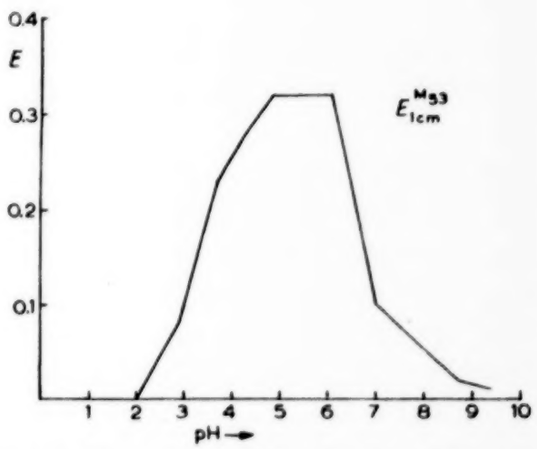


Fig. 3. The influence of pH on the extinction of the complex UO_2^{+2}–reagent I. c = 138 μg U(VI)/10 ml.

SUMMARY

A new, very sensitive reagent is proposed for the colorimetric determination of uranium(VI), namely 1-phenyl-3-methyl-4-(3′-carboxy-4′-hydroxyphenyl-azo)-pyrazol-5-one.

RÉSUMÉ

Le 1-phényl-3-méthyl-4-(3′-carboxy-4′-hydroxyphényl-azo)-pyrazol-5-one est proposé comme réactif pour le dosage colorimétrique de l'uranium(VI).

ZUSAMMENFASSUNG

Das 1-Phenyl-3-methyl-4-(3′-carboxy-4′-hydroxyphenyl-azo)-pyrazol-5-one wird als neues Reagenz für die colorimetrische Bestimmung von Uran vorgeschlagen.

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UTILISATION DE L'ACIDE PHÉNYLARSONIQUE EN TURBIDIMÉTRIE

DOSAGE DU TANTALE

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INTRODUCTION

On détermine habituellement de faibles quantités de tantale par une colorimétrie de son composé avec le pyrogallol[1]. Cette méthode, étant peu spécifique, nécessite des séparations. La plus utilisée est, à l'heure actuelle, l'extraction du fluorure par l'hexone en divers milieux[1-4]. Mais cette séparation a pour but principal d'éliminer l'interférence du niobium; l'effet d'autres éléments a été peu étudié. On connaît par contre, la spécificité de l'acide phénylarsonique en milieu acide[5]; MAJUMDAR[6] a étudié la séparation gravimétrique de quantités pondérales de tantale et de niobium par ce réactif. Nous avons mis au point une méthode de dosage turbidimétrique par l'acide phénylarsonique, suffisamment sélective pour éliminer la plupart des séparations, et nous avons appliqué cette méthode au cas particulier d'un alliage uranium-tantale contenant de 0.5 à 2% de tantale.

ÉTUDE DE LA TURBIDIMÉTRIE

Réactifs

Acide phénylarsonique en solution aqueuse à 2%; glycérine en solution aqueuse à 50%.

Solutions étalons

Solution de sulfate d'uranyle à 100 g U/l; solution de niobium, 500 mg/l de niobium dans une solution à 5% d'acide tartrique; solution de tantale à 1 g/l obtenue par attaque nitrofluorhydrique du métal et élimination de l'acide fluorhydrique par évaporation en présence d'acide sulfurique; solution de zirconium à 100 mg/l obtenue par dissolution dans H_2SO_4 2 *N* d'oxychlorure de zirconium „MERCK".

Mode opératoire

Dans une fiole de 10 ml, introduire environ 200 μg de Ta; acidifier par 1 ml d'acide sulfurique 12 *N*, ajouter 1 ml de la solution de stabilisant (glycérine), puis 1 ml d'acide phénylarsonique; compléter à 10 ml; bien agiter; déterminer la transmission au spectrophotomètre après 1/2 h d'attente.

Stabilisation du précipité

La glycérine nous a donné les meilleurs résultats: l'absorption due au précipité est

constante pendant au moins une heure. Avec la gomme arabique les points s'alignent mal et la sensibilité est plus faible. La gélatine (1 ml à 10%) empêche toute précipitation.

Courbes de transmission et choix de la longueur d'onde

En utilisant le mode opératoire décrit, on a déterminé les courbes de transmission de: 200 μg Ta, 50 μg Zr, 100 mg U, 100 mg U + 50 μg Zr.

Les résultats concernant les différentes solutions sont rassemblés dans le Tableau I et la Fig. 1. La cuve de référence contient de l'eau; la largeur de fente est égale 0.18 mm à 310 mμ avec une lampe à tungstène.

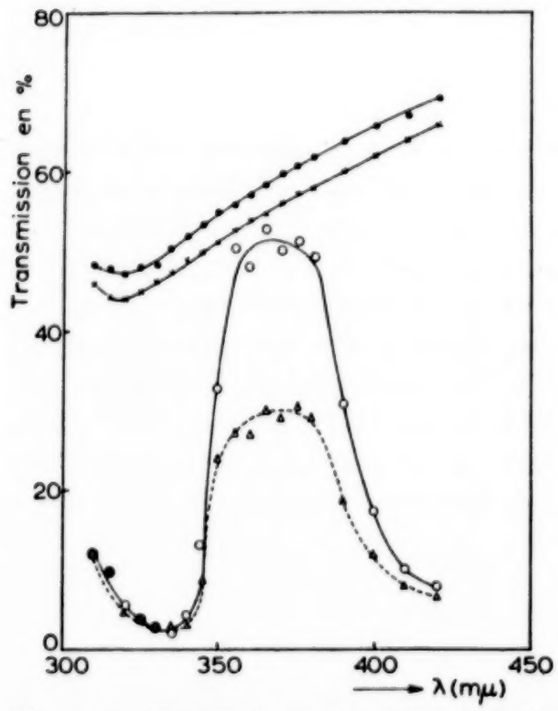

Fig. 1. Turbidimétrie du zirconium et du tantale à l'acide phénylarsonique. Courbes de transmission: ● = 50 μg Zr; × = 200 μg Ta; ○ = 100 mg U; △ = 50 μg Zr + 100 mg U.

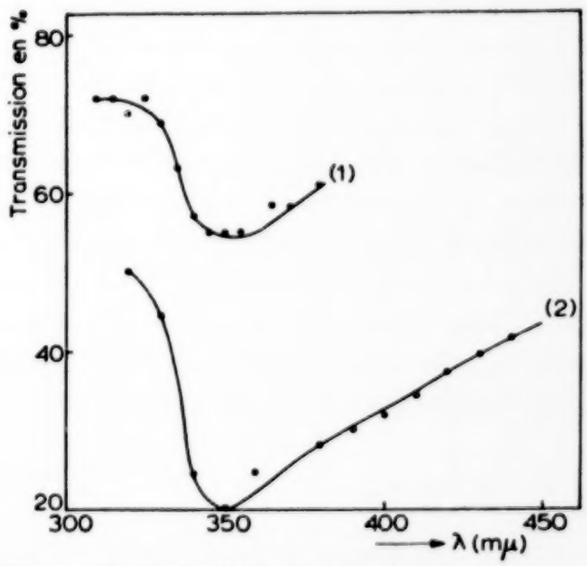

Fig. 2. Turbidimétrie du tantale et du zirconium à l'acide phénylarsonique. Courbes d'absorption en présence d'U. Courbes d'absorption: cuve de référence le „blanc et l'uranium", 1 = 50 μg Zr + 100 mg U; 2 = 500 μg Ta + 100 mg U.

L'examen de ce tableau montre immédiatement que le dosage sera possible seulement dans la zone 350–370 mμ. Pour nous en convaincre, nous allons tracer les courbes de transmission en utilisant dans la cuve de référence une solution contenant tous les réactifs et 100 mg d'uranium. Nous aurons cette fois le minimum de transmission dû au zirconium ou au tantale seuls. Cette courbe ne sera pas comparable aux précédentes parce que la présence d'uranium dans la cuve de référence nous oblige à utiliser une fente beaucoup plus large (0.49 mm) (*cf.* Tableau II et Fig. 2).

Cette fois, le minimum de transmission est visiblement à 350 mμ. Ces conditions sont celles du dosage en présence d'uranium. On a vérifié que la courbe d'étalonnage du tantale en présence d'uranium, est superposable à celle du tantale seul, à cette longueur d'onde (Fig. 3).

TABLEAU I

COURBES DE TRANSMISSION PAR RAPPORT À L'EAU

mμ	Transmission en %			
	Ta	Zr	U	U + Zr
310	46	48.5	12	12
315	44.5	48	8	8
320	44.5	47.5	5.5	5
325	45	48	4	4
330	46.5	48.5	3	3
335	47.5	50.5	2.5	3
340	49	52	4.25	3.5
345	50	53.5	13.25	9
350	51.5	58	33	24
355	53	56	50.5	27.5
360	54	57.5	48	27
365	55	58.5	53	30
370	56.5	60	50.5	29.5
375	57.5	61	51.5	30.5
380	58	62	49	29
390	60	64	31	19
400	62	66	17.5	12
410	64	67.5	10.5	8
420	66	69.5	8	7

TABLEAU II

COURBES DE TRANSMISSION PAR RAPPORT À L'URANIUM

λ mμ	Transmission en %	
	50 μg Zr	300 μg Ta
310	72	
315	72	
320	70	50
325	72	
330	69	44.5
335	63	
340	57	24.5
345	55	
350	55	20
355	55	
360	55	24.5
365	58.5	
370	58.5	26
380	61.5	28
390		30
400		32
410		34.5
420		37.5
430		39.5
440		41.5
450		43

Influence de l'acidité

Le domaine de précipitation du composé se situe en milieu sulfurique, à une nor-

malité comprise entre 1.2 et 3.0 *N*. Aux faibles acidités (<1.2 *N*), les petites quantités de tantale (<200 μg) ne précipitent pas. Au-delà de 3 *N*, on n'observe pas de précipité même avec 500 μg de Ta.

Ions gênants

Ce sont essentiellement le zirconium et le niobium parmi les cations; les fluorures parmi les anions.

Le zirconium: pris isolément, son domaine de précipitation en milieu sulfurique est étroit: 0.2 à 0.6 *N*. Mais en présence de tantale il y a un entraînement de Zr même à des acidités plus élevées, ainsi qu'en témoigne le Tableau III.

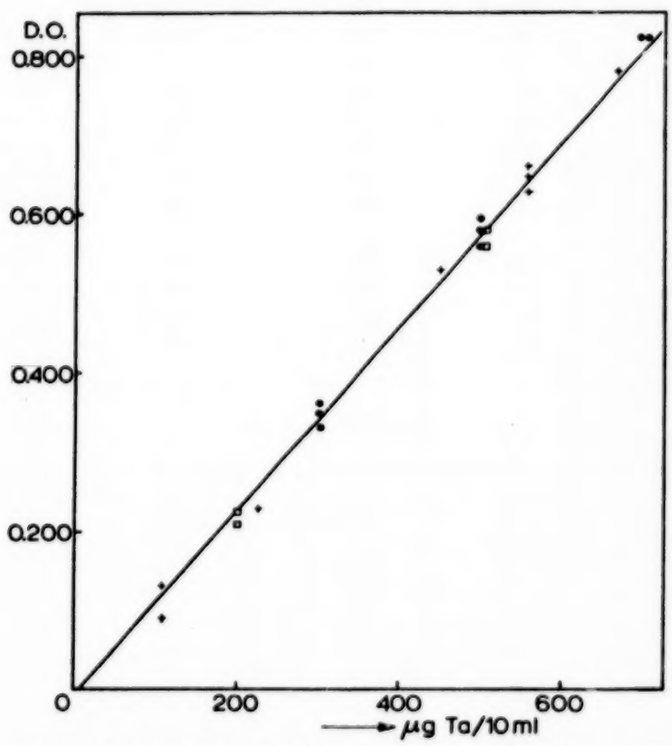

Fig. 3. Courbe d'étalonnage. Ta par turbidimétrie à l'acide phénylarsonique (milieu H_2SO_4 2 *N*). λ = 350 mμ; ● = Ta seul; +, □ = Ta + U.

TABLEAU III

INFLUENCE DE L'ACIDE SULFURIQUE SUR L'INTERFÉRENCE DE Zr

mg U	*μg Zr*	*μg Ta*	*H_2SO_4 normalité*	*Densité optique*	*Erreur %*
50	0	200	1.14	0.225	+ 2.5
50	0	200	2	0.215	— 2.5
50	50	200	1.24	0.220	0
50	100	200	1.10	0.240	+10
50	200	200	1.24	0.400	+90
50	200	200	2	0.230	+ 5
50	500	200	2	0.240	+10
50	500	200	2.3	0.230	+ 5

Nous considérerons qu'une erreur de 5% est dans les limites d'une méthode turbidimétrique et pouvons conclure que l'on peut tolérer un rapport moléculaire Zr/Ta $\leqslant 5$. Par contre, il a été impossible d'éviter la coprécipitation de 1 mg de Zr (les complexants comme l'acide tartrique sont inefficaces à cette acidité; les fluorures empêchent la précipitation de Zr, mais aussi celle de Ta).

Le niobium: on utilise pour éliminer l'interférence du niobium, son complexe avec l'eau oxygénée. En prenant comme erreur relative admissible 5%, il est possible de tolérer un rapport moléculaire: Nb/Ta = 1.

DOSAGE D'UN ALLIAGE URANIUM–TANTALE DE TENEUR EN TANTALE > 0.2%

Attaque

Pour 1 g d'alliage, verser 3 ml d'acide sulfurique 12 *N*, puis 5 ml d'acide nitrique concentré. Chauffer légèrement, puis ajouter goutte à goutte 0.5 ml d'acide fluorhydrique concentré jusqu'à attaque complète. Ajouter, si cela est nécessaire, un peu d'eau pour éviter la cristallisation des sels, ou de l'acide fluorhydrique si l'attaque est lente. Quand l'attaque est terminée ajouter avec précaution 14 ml d'acide sulfurique concentré et porter à fumées blanches 10 min. Laisser refroidir et selon la teneur en tantale, amener à un volume convenable.

TABLEAU IV

RÉSULTATS DE DOSAGE

Echantillon No.	*Prise d'essai*	*Densité optique*	*µg Ta dans la partie aliquote*	*% Ta dans l'alliage*
1	400 mg alliage	0.285	250	0.62 ± 0.01
	800 mg alliage	0.565	496	
	400 mg + 91 µg Ta	0.390	342 — 91 = 251	
	400 mg + 273 µg Ta	0.595	518 — 273 = 245	
2	400 mg alliage	0.470	410	1.05 ± 0.02
	400 mg + 91 µg Ta	0.570	498 — 91 = 407	
	400 mg + 182 µg Ta	0.685	596 — 182 = 414	
3	400 mg alliage	0.340	298	0.73 ± 0.02
	200 mg alliage	0.170	149	
	400 mg + 91 µg Ta	0.445	388 — 91 = 297	
	400 mg + 182 µg Ta	0.530	462 — 182 = 280	
4	200 mg alliage	0.475	416	2.07 ± 0.04
	200 mg + 91 µg Ta	0.585	508 — 91 = 417	
	200 mg + 273 µg Ta	0.790	686 — 273 = 413	

Dosage

Prendre une partie aliquote contenant moins de 700 µg de tantale.

1. Acidifier à l'acide sulfurique (environ 1 ml de H_2SO_4 12 *N*) de telle sorte que la solution finale soit entre 2 *N* et 3 *N*. Ajouter 1 ml de H_2O_2 à 2% (s'il y a du niobium).

2. Ajouter 1 ml de la solution de glycérine, puis 1 ml de la solution d'acide phénylarsonique.

3. Préparer dans les mêmes conditions un essai à blanc avec la même quantité d'uranium (ne contenant pas de tantale) pour la cuve de référence.

4. Faire un essai sur une partie aliquote en ajoutant tous les réactifs sauf l'acide phénylarsonique. Ce deuxième essai à blanc permet de déduire les absorptions dues aux éléments formant un complexe avec H_2O_2.

5. Faire également deux essais en ajoutant des quantités connues de tantale.

6. Après une demi-heure d'attente, déterminer la densité optique à $\lambda = 350$ mμ.

7. Déduire de la densité optique trouvée pour l'échantillon la somme des densités optiques dues aux deux essais à blanc.

8. Enfin, déterminer la quantité de tantale présente dans l'échantillon, d'après la droite d'étalonnage obtenue en ajoutant des quantités connues de tantale à la solution d'attaque. Cette droite doit être identique à la droite obtenue par turbidimétrie de la solution étalon de tantale.

Précision

Une teneur en tantale de 0.2 à 2% peut être déterminée avec une erreur relative $< \pm 5\%$ (*cf.* résultat Tableau IV).

Note

En présence de fer(III), il est nécessaire d'ajouter un peu d'acide ascorbique.

RÉSUMÉ

On décrit le dosage turbidimétrique du tantale par l'acide phénylarsonique. La méthode est rapide et nécessite rarement une séparation préliminaire. Les seuls éléments gênants sont le zirconium et le niobium, pour lesquels on peut tolérer des rapports molaires, au plus égaux à: Nb/Ta = 1 et Zr/Ta = 5.

SUMMARY

A turbidimetric method is described for the determination of tantalum with phenylarsonic acid. The method is fast and rarely requires preliminary separation. The only interfering elements are zirconium and niobium when present in molar ratios greater than Nb : Ta = 1 and Zr : Ta = 5.

ZUSAMMENFASSUNG

Beschreibung einer nephelometrischen Methode zur Bestimmung von Tantal mit Phenylarsonsäure. Die Methode ist rasch und erfordert nur in wenigen Fällen einen Trennungsprozess. Störende Elemente sind Zirkonium und Niob, wenn sie eine gewisse Konzentration überschreiten.

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THE RAPID SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN NON-FERROUS ALLOYS

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INTRODUCTION

When copper determinations are required on a variety of materials such as non-ferrous alloys and corrosion products, several different methods are often employed. A survey of the literature on this subject revealed that many of the methods require rather critical reaction conditions often with specialised reagents after initial separation of the copper or of interfering elements. It was considered that many advantages would be gained if one simple method could be developed which would be applicable to a variety of alloys and materials. It was thus decided to develop a spectrophotometric method involving no separations and utilising a simple reaction to produce a self-colouring copper ion. Preliminary experiments showed that cupric chloride formation in strong hydrochloric acid solution would produce a sufficiently sensitive reaction, but this system has been little exploited and has been used by relatively few workers[1-5].

EXPERIMENTAL

Apparatus and reagents

All reagents were of the "AnalaR" quality where possible, and optical density measurements were made in glass cells on a Unicam S.P.600 spectrophotometer.

Absorption spectra

In order to assess the sensitivity of the cupric chloride system, and the types of interference likely to be met, absorption spectra were plotted for the chlorides of copper, nickel, iron, chromium and cobalt in strong hydrochloric acid solution. These spectra are reproduced in Fig. 1, and more detailed spectra for cupric chloride are shown in Fig. 2. The cupric chloride shows intense absorption at 385 mμ and a less intense absorption at 950 mμ. The absorption characteristics of these "self-colouring" ions are summarised in Table I, from which it is obvious that minimum interference will occur with measurements at the 950-mμ peak. The only serious interference likely to be met is cobalt, but this must be in appreciable amounts, and as such, is not often encountered in the alloys under consideration. Measurement at the 950-mμ peak enables copper concentrations down to 10 μg/ml to be determined.

TABLE I

ABSORPTION MAXIMA

E = molecular extinction coefficient

Metal	*mμ*	*E*	*mμ*	*E*	*mμ*	*E*
Cu^{+2}	385	1360	950	104		
Co^{+2}	625	354	660	531	690	572
Ni^{+2}	410	8	760	3		
Cr^{+3}	460	27	650	21		
Fe^{+3}	360	2940				

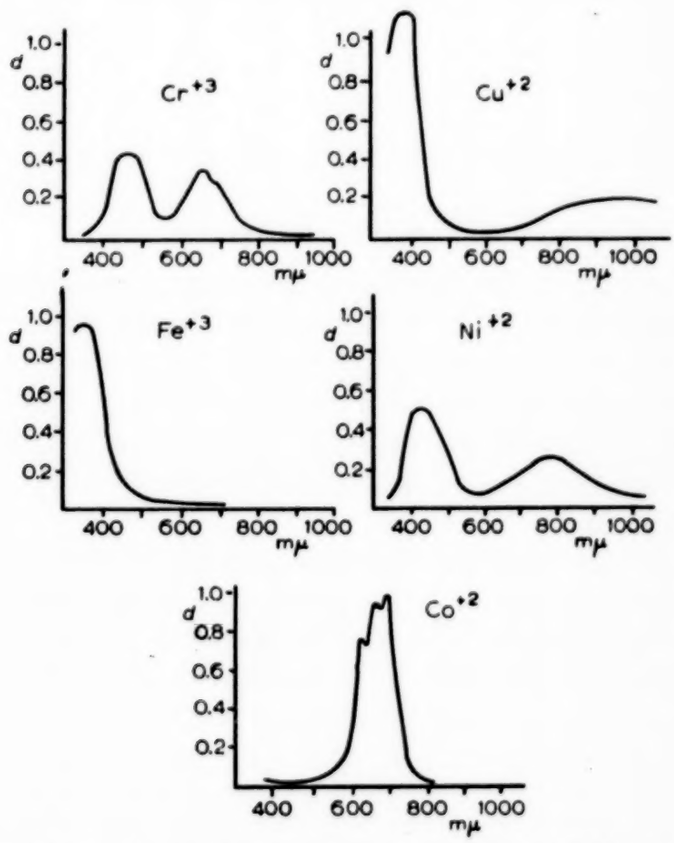

Fig. 1. Absorption spectra in concentrated HCl.

Acid concentration

The controlling factor is the hydrochloric acid concentration. The effects of this were investigated using copper concentrations from 0.125 to 5 mg/ml with appropriate cell widths to accommodate this range. The results obtained are plotted in Fig. 3. The effect of acidity is independent of copper concentration. Up to an acid concentration of 325 g hydrochloric acid per litre a rapid linear increase in absorption occurs. At concentrations above this, however, the effect is very much less pronounced. At the high acidities a variation of $\pm$10 g hydrochloric acid per litre produced an error in optical density reading of only $\pm$0.005. To maintain errors in this range the acid concentration was controlled by sp.gr. measurement of the stock acid. The "AnalaR" acid has a nominal sp.gr. of 1.18 and if the stock acid is maintained between sp.gr. 1.177 and 1.184 (by hydrometer at 20°) then the concentration will be between 418 to 438 g hydrochloric acid per litre[6]. In practice it has been found that the "AnalaR" acid requires no adjustment.

Effects of nitric acid

Nitric acid is often employed to facilitate dissolution of many samples and it was decided to investigate the effects of this acid on the absorption of the cupric chloride. It was found that up to at least 15% by volume of concentrated nitric acid could be

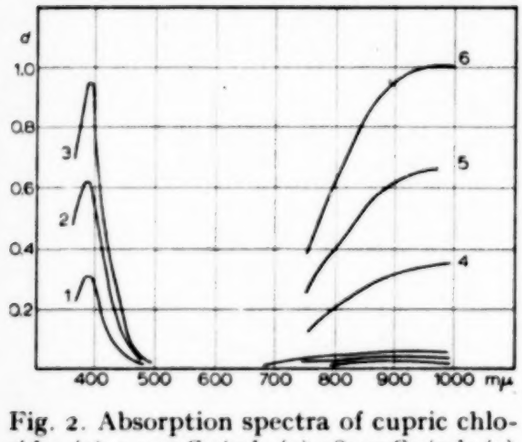

Fig. 2. Absorption spectra of cupric chloride. (1) 14 μg Cu/ml; (2) 28 μg Cu/ml; (3) 42 μg Cu/ml; (4) 200 μg Cu/ml; (5) 400 μg Cu/ml; (6) 600 μg Cu/ml.

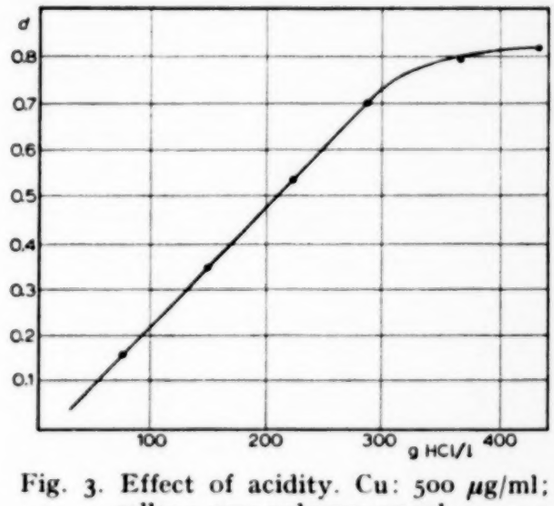

Fig. 3. Effect of acidity. Cu: 500 μg/ml; cells: 1 cm; volume: 10 ml.

tolerated in the final solution without any effects on the optical density readings. However, with this amount of nitric acid present, a continuous undesirable gas evolution occurs, and it is thus preferable to remove the bulk of any nitric acid used by a single evaporation with hydrochloric acid during processing of samples.

Stability and temperature effects

Solutions, in stoppered flasks, were stable for at least three days, and temperature changes over the range 18° to 35° had no effect on the optical density readings.

TABLE II

REPRODUCIBILITY

Cu(mg/ml)	*Cell width (cm)*	*Mean density*	*Maximum deviation*
0.005	4	0.040	0.001
0.05	4	0.360	0.001
0.05	1	0.088	0.002
0.1	1	0.188	0.002
0.25	1	0.446	0.005
0.5	1	0.900	0.010

Reproducibility

To check the reproducibility of preparation and measurement, known amounts of copper were processed, and optical density readings taken. The results obtained, for five samples in each case, are summarised in Table II.

The reproducibility was found to be satisfactory over a copper concentration range of 50:1 and still adequate over a 100:1 range.

Effects of other elements

To test the effects of other elements, standard solutions of these were added to standard amounts of copper. In all cases the solutions were evaporated and processed to yield final solutions in concentrated hydrochloric acid. The results obtained are summarised in Table III.

TABLE III

TOLERANCE TO OTHER ELEMENTS

Cu present = 0.5 mg per ml

5%	10%	30%	50%	100%
Hg^{+2} [a]	As^{+3} [a]	Zn^{+2}	Sb^{+3} [a]	Al^{+3} [a]
	Ba^{+2} [a]		Bi^{+3}	Mg^{+2} [a]
	Be^{+2} [a]		Cd^{+2}	Ni^{+2} [a]
	Ca^{+2} [a]		Cr^{+3} [a]	Sn^{+4} [a]
	Ce^{+4} [a]		Mn^{+2} [a]	Fe^{+3} [a]
	PO_4^{-3} [a]		Ag^{+1} [b]	Pb^{+2} [a]
	TeO_4^{-2} [a]		Ce^{+3} [a]	
	W^{+6} [b]			
	V^{+5} [a]			
	Zr^{+2} [a]			

Valencies are those as added to test solution; tolerances expressed as per cent ratio to Cu.
[a] amounts greater than those shown were not investigated.
[b] precipitation, but no interference occurred after centrifuging.

As a further test, calibrations were carried out using tin, lead, aluminium, zinc, magnesium, and nickel as "base metals", with copper added as standard solution. Thus, in each case 0.05 g of pure "base metal" was taken and increments of copper solution were added to cover a range up to 10% copper. In every case conformity to Beer's Law was obtained, and optical density readings reproduced within a maximum of 1.5% of the mean. Thus, for non-ferrous analysis one calibration with copper solution will suffice for a variety of alloys, *e.g.* tin–lead, nickel, aluminium, zinc and aluminium alloys, etc.

Calibration

The following standard solutions are suitable for calibration.

Solution 1, 1 ml ≡ 2 mg Cu. Dissolve 1 g of pure copper in a minimum of nitric acid. When dissolved evaporate to dryness. Allow to cool, then dissolve the residue in cold concentrated hydrochloric acid ($d = 1.18$) finally diluting to 500 ml with this acid.

Solution 2, 1 ml ≡ 0.2 mg Cu. Dilute 50 ml of solution *1* to 500 ml with concentrated hydrochloric acid ($d = 1.18$). Calibration data, using these solutions, are given in Tables IV and V. Table IV shows the ranges and dilutions etc. and then reference to Table V gives the additions of standard copper solutions together with the equivalent copper contents.

In all cases measure the required volume of standard copper solution into 20-, 50- or 100-ml graduated flasks, as appropriate, and dilute to volume with concentrated hydrochloric acid ($d = 1.18$). Measure the optical densities of these solutions at 950 mμ in the appropriate cells and plot density against % Cu, when linear calibrations should be obtained.

TABLE IV

	A	*B*	*C*	*D*	*E*
Cu content (%)	0–2	to 5	to 10	to 50	to 100
Sample wt. (g)	0.1	0.05	0.05	0.05	0.05
Final vol. (ml)	20	20	50	50	100
Cell width (cm)	4	4	4	1	1
Copper soln. No.	2	2	2	1	1

TABLE V

ml OF STANDARD Cu SOLUTION AND CORRESPONDING %Cu

A		*B*		*C*		*D*		*E*	
ml	*% Cu*	*ml*	*% Cu*	*ml*	*% Cu*	*ml*	*% Cu*	*ml*	*% Cu*
2	0.4	2.5	1	5	2	2.5	10	5	20
4	0.8	5.0	2	10	4	5.0	20	10	40
6	1.2	7.5	3	15	6	7.5	30	15	60
8	1.6	10.0	4	20	8	10.0	40	20	80
10	2.0	12.5	5	25	10	12.5	50	25	100

Analytical procedure

As a result of the investigations carried out, the following procedure has been established for the determination of copper in samples of alloys, etc. Since the method is applicable to a wide variety of samples, individual treatment for dissolution can be varied, but the following method can be taken as being typical. The sample weights, final volumes and cell widths to cover different ranges of copper contents can be chosen from Table IV.

Transfer the sample to a 100-ml beaker, and attack with hydrochloric acid, added dropwise. Complete the dissolution of the sample by addition of concentrated nitric acid. Evaporate to dryness, taking care to avoid baking. Allow the residue to cool, then dissolve, in the cold, in about 5 ml of concentrated hydrochloric acid ($d = 1.18$). If any insoluble compounds appear, transfer to a centrifuge tube, washing with a minimum of cold concentrated hydrochloric acid. Spin off insoluble matter, then dilute and wash the solution to the required standard volume with the hydrochloric acid. Measure the optical density of the solution at 950 mμ using the hydrochloric acid as compensating solution. Calculate the copper content of the sample by reference to the calibration curves.

Accuracy

The accuracy of the method was checked by analysing several British Chemical Standard samples, the results obtained being summarised in Table VI.

These results showed that both accuracy and reproducibility are quite adequate.

DISCUSSION

The procedure which has been evolved is very simple, and shows many advantages over other methods using somewhat specialised reagents. Many different types of samples have been analysed by this method in this laboratory, including non-ferrous alloys on a control basis and corrosion and breakdown deposits. One advantage in dealing with corrosion products, etc. is that the reaction is sufficiently sensitive to enable a small sample to be used, and at the same time the final solution is not con-

TABLE VI

RESULTS ON STANDARD SAMPLES

British Chemical Standards (B.C.S.) used

Standard	*Certified % Cu*	*% Cu found Mean of 10*	*Standard deviation*	*Coefficient of variation*
White metal 'A'	0.33	0.35	±0.008	± 2.3
White metal 'B'	4.08	4.13	±0.067	± 1.6
Cupro nickel "A"	68.76	68.3	±1.06	± 1.5
Mn brass "B"	58.9	58.4	±1.55	± 2.7
Al alloy 181	4.64	4.73	±0.033	± 0.7
Mg/Al alloy	0.13	0.14	±0.024	±17.1

taminated with reagents. Thus, after evaporation of excess acid, further analyses can be carried out on the same solution. Although satisfactory results have been obtained on samples of high copper contents, the method is not recommended where copper is the major constituent. In such cases a differential spectrophotometric technique using perchloric acid is used. However, the method does enable rapid classification to be made in such cases. With some samples, precipitation of insoluble compounds such as silica, tungsten oxide, silver chloride, etc. occurs, but no errors have been observed when these have been removed by centrifuging and washing with concentrated hydrochloric acid.

Although relatively large amounts of iron do not interfere, it has been found that the method is not directly applicable to the determination of copper in irons and steels. For these samples the reaction with diquinolyl followed by amyl alcohol extraction is used. As an indication of the sensitivity of the simple chloride reaction, a copper concentration of 10 μg per ml can be measured at 950 mμ. On the Unicam S.P. 600 instrument this produces an optical density of approximately 0.1 when using a 4-cm cell.

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SUMMARY

A very simple method has been established for the rapid determination of copper, employing the formation of the chlorocupric anion by means of concentrated hydrochloric acid. The absorption of the chlorocupric anion is measured spectrophotometrically at a wavelength of 950 mμ. The method is applicable to a wide variety of samples, including many non-ferrous alloys.

RÉSUMÉ

Une méthode spectrophotométrique, rapide et très simple, est proposée pour le dosage du cuivre dans divers alliages. On utilise l'acide chlorhydrique comme réactif et on mesure l'absorption de l'anion chlorocuprique formé.

ZUSAMMENFASSUNG

Beschreibung einer raschen und einfachen spektrophotometrischen Methode zur Bestimmung von Kupfer. Sie beruht auf der Messung der Absorption des Chlorokupfer Anions.

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THE SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF CERIUM

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The majority of methods available for the colorimetric determination of cerium depend on the oxidising properties or colour of ceric solutions. Cerous ion can be oxidised by persulphate in hot acidic solution in the presence of catalytic amounts of silver ion. The yellow colour of the resulting ceric solution is sufficiently intense for the determination of milligram amounts of cerium[1-3]. A rather more sensitive procedure depends on the yellow colour which is formed when a cerous salt is treated with potassium carbonate in the presence of air or hydrogen peroxide[4-6]. In acid solution, ceric ion oxidises a number of organic compounds, such as brucine[7], sulphanilic acid[8], benzidine[9,10], and the leucobase of malachite green[11], to coloured compounds which can be used for the photometric determination of the element.

GORDON AND FEIBUSH[12] have described an indirect method for the determination of cerium, in which ceric ion, formed by oxidation with lead dioxide, was treated with excess ferrous sulphate solution; excess ferrous ion remaining was determined photometrically with 1,10-phenanthroline. When this method was tested using microgram amounts of cerium very variable results were obtained; this variability was attributed to the difficulty of completely removing traces of suspended lead dioxide from the solution and to oxidation of ferrous ion before addition of the complexing agent. Attempts were therefore made to oxidise the cerous ion by means of persulphate in the presence of silver ion as catalyst. It was found that complete oxidation of up to 80 μg of Ce^{+3} in 4 ml of 0.3 *N* sulphuric acid occurred when the solution was heated in a boiling water bath for 5 min with 1 ml of 0.2% ammonium persulphate, in the presence of 50 μg of silver ion (added as silver sulphate). Under these conditions excess of persulphate was completely decomposed in 5–7 min. If the solution was boiled on a hot plate oxidation of cerium was incomplete.

SANDELL[13] has suggested that ceric–cerium could be estimated by treating the sample with excess of a solution of the red ferrous–phenanthroline complex: The decrease in optical density of the solution, caused by the oxidation of the ferrous complex to the faintly coloured ferric–phenanthroline complex, would be an indirect measure of the cerium present. In this method the ferrous iron added would be stabilised by the phenanthroline. It would therefore be less likely to be oxidised by the

* This work was carried out in partial fulfillment of the requirements for the degree of Ph.D. (London).

oxygen, with which the solution is super-saturated, than if the ferrous solution was added separately as described by GORDON AND FEIBUSH[12].

The ferrous–phenanthroline complex is completely stable over the pH range 2–9. At pH values below 2, the complex is partly decomposed and its colour is much weaker. When ferrous–phenanthroline reagent was added to a blank solution which had been treated with persulphate as described above, the low pH of the resultant solution (<1) caused rapid fading of the colour. Since cerous hydroxide precipitates at pH 2.5, the range usable for the determination of cerium is limited to pH 2.0–2.4. It was found that if the solution was buffered to pH 2.3 with sodium acetate, the colour was stable for about 1 h.

The sensitivity of the method can be doubled if sulphonated bathophenanthroline[14] is substituted for phenanthroline in the reagent.

DETERMINATION OF CERIUM

Reagents

Silver sulphate solution (100 μg Ag^+/ml). Prepare a solution containing 0.1445 g of silver sulphate per l.

Ammonium persulphate solution. Dissolve 1 g of ammonium persulphate in 50 ml of water. Since this reagent is unstable it should be prepared freshly immediately before use.

Ferrous–phenanthroline reagent. Dissolve 1.0 g of 1,10-phenanthroline and 0.0653 g of ferrous ammonium sulphate in 250 ml of 0.1 *N* sulphuric acid. This solution has an optical density of *ca.* 7.0 at 510 mμ in a 1-cm cell and 1 ml contains 37.2 μg of Fe^{+2}, which is equivalent to *ca.* 93 μg of Ce^{+4}. This reagent contains a ninefold excess of phenanthroline over the amount required to combine with the ferrous ion present.

Sodium acetate (4.5 *M*). Dissolve 153 g of sodium acetate trihydrate in water and dilute to 250 ml.

Standard cerium solution. Digest 0.1228 g of pure cerium dioxide overnight with 10 ml of concentrated sulphuric acid at 270°. Dilute with 100 ml of water and add 0.5 ml of 30% hydrogen peroxide. Boil until all the solid has dissolved and excess hydrogen peroxide has been destroyed. When cold, dilute to 250 ml. This stock solution contains 400 μg Ce^{+3}/ml. Prepare a working solution containing 10 μg of Ce^{+3}/ml from it as required.

Method

Pipette into a 25-ml conical flask 4 ml of the solution to be analysed (containing not more than 80 μg of cerium, and having an acidity not greater than 0.1 *N*). Add 0.13 ml of concentrated sulphuric acid (s.g. 1.84), 0.5 ml of silver sulphate and 1 ml of ammonium persulphate solution. Immerse the flask to about half its height in a bath of boiling water for 10 min. After cooling, transfer the solution to a 10-ml graduated flask, using not more than 2 ml of water for washing out the conical flask. Add 1 ml of ferrous–phenanthroline reagent followed by 1 ml of 4.5 *M* sodium acetate solution. Mix well and dilute to 10 ml with water. Measure the optical density of the solution at 510 mμ in a 1-cm cell within 30 min of mixing. Carry out a blank determination in the same manner, using 4 ml of water instead of the sample. Calibrate the method using 4 ml of the dilute standard cerium solution (40 μg Ce^{+3}).

Calibration curve and reproducibility

The linearity of the calibration curve was checked by treating various amounts of cerous sulphate as described above. The results are given in Table I and show that the decrease in optical density of the solutions as compared with the blank is proportional to the weight of cerium up to about 80 μg.

TABLE I

CALIBRATION OF METHOD WITH KNOWN AMOUNTS OF CERIUM

Wt. of Ce (μg)	*Optical density*[a]	*Mean decrease in optical density*	*Decrease per 10 μg Ce*
0	0.741 0.739		
20	0.602 0.602	0.138	0.0690
40	0.458 0.458	0.282	0.0705
50	0.387 0.385	0.354	0.0708
60	0.318 0.316	0.423	0.0705
80	0.158 0.147	0.582	0.0727

[a] at 510 mμ, 1-cm cell

In order to test the reproducibility of the method replicate determinations were carried out on 50-μg samples of cerium. The following optical density decreases were observed: 0.350, 0.360, 0.352, 0.344, 0.364, 0.359; mean 0.355; standard deviation 0.007; coefficient of variation 2.0%.

Interference of foreign ions

The interference of a number of ions was investigated by carrying out the persulphate oxidation stage on them and then treating with ferrous–phenanthroline reagent as described above. The following ions were found to cause no interference: Pb^{+2}, Na^{+}, K^{+}, Ca^{+2}, Mg^{+2} (20 mg of each), Al^{+3}, Fe^{+3}, Ti^{+4} (10 mg of each), Ag^{+}, Be^{+2}, Cd^{+2}, Co^{+2}, Cu^{+2}, Hg^{+2}, Ni^{+2}, Zn^{+2}, MoO_4^{-2}, ReO_4^{-}, SeO_4^{-2}, TeO_4^{-2} (1 mg of each), Ga^{+3} (200 μg), Gd^{+3}, Ge^{+4}, In^{+3}, La^{+3}, Sc^{+3}, Tl^{+}, UO_2^{+2} (100 μg of each).

Serious interference is experienced with ions which can either oxidise the ferrous–phenanthroline reagent directly, or which can be oxidised by persulphate to strong oxidising agents. Traces of chromium and manganese must be absent since they are oxidised by persulphate to chromate and permanganate respectively. Chromium can be removed by volatilisation as chromyl chloride; manganese is most conveniently separated by ion exchange[15]. Vanadate also interferes slightly; 1 mg of VO_3^{-} is equivalent to *ca.* 14 μg of cerium.

Chloride, oxalate, citrate and tartrate interfere by reducing the ceric salt. Considerable interference is caused by fluoride which bleaches the ferrous–phenanthroline complex. The presence of even traces of perchlorate leads to cloudiness of the solution owing to the precipitation of slightly soluble phenanthroline perchlorate. If any of

these interfering anions are present in the solution to be analysed they should be removed by fuming to dryness twice with concentrated sulphuric acid.

SUMMARY

A spectrophotometric procedure, which has a coefficient of variation of *ca.* 2%, is described for the determination of up to 80 μg of cerium. Ceric ion formed by oxidation with persulphate, in the presence of catalytic amounts of silver, is reduced to the cerous state by treatment with excess ferrous–phenanthroline reagent. The decrease in optical density of the ferrous–phenanthroline compared with the reagent blank is a measure of the amount of cerium present. The only common cations which cause serious interference are Mn^{+2} and Cr^{+3}.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage du cérium. On procède par oxydation du cérium au moyen de persulfate, en présence d'argent comme catalyseur. Puis on traite la solution à analyser par la phénanthroline ferreuse et on mesure la diminution de la densité optique, en comparant à un essai à blanc.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Cerium. Ce(IV) wird mit einem Überschuss von Eisen(II)–Phenanthrolin reduziert und die Abnahme der optischen Dichte der Eisen(II)–Phenanthrolinlösung gemessen.

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DOSAGE DE L'ACIDE TARTRIQUE ET DES TARTRATES PAR LE TÉTRACÉTATE DE PLOMB

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Pour le dosage oxydimétrique de l'acide tartrique on se sert d'agents oxydants énergiques comme par exemple le permanganate alcalin[1-3], les composés du cérium tétravalent[4-6], le bichromate[7,8], l'iodate[9,10], le periodate[11,12], le vanadate[13-16] ou bien de composés de cuivre trivalent[17,18]. Dans la plupart des cas, il est nécessaire d'ajouter un excès de réactif et de chauffer, plus ou moins longtemps.

Lors de notre étude, nous avons constaté que l'oxydation de l'acide tartrique par le tétracétate de plomb s'effectue à la température du laboratoire, en présence d'acétate alcalin, en milieu d'acide acétique à 80%, rapidement et quantitativement avec formation d'anhydride carbonique et d'eau.

Nous avons pu fixer la durée d'action à 30 min en utilisant un excès de réactif. La quantité non utilisée de tétracétate de plomb est déterminée par un titrage potentiométrique au moyen d'une solution d'hydroquinone. Ces deux solutions (tétracétate de plomb et hydroquinone) sont très stables. La vitesse, la précision et même la simplicité d'exécution du procédé proposé dépassent celles de la plupart des méthodes oxydimétriques utilisées jusqu'à présent.

PARTIE EXPÉRIMENTALE

Réactifs

Acide sulfurique, acide acétique, acétate de potassium, tartrate double de sodium et de potassium, tartrate acide de potassium (p.a. Merck, Lachema).

$Na_5Bi(C_4H_2O_6)_2 \cdot 9H_2O$, $Na_5Bi(C_4H_2O_6)_2 \cdot 6H_2O$, $K_5Bi(C_4H_2O_6)_2 \cdot 4H_2O$, $Li_5Bi(C_4H_2O_6)_2 \cdot 8H_2O$ et $BiC_8H_9O_{12}$ ont été préparés au laboratoire*.

Solution d'acide tartrique 0.005 *M*, titrée par le periodate de potassium[12]. Solution de tétracétate de plomb 0.05 *M* dans l'acide acétique glacial (exempt de plomb(II)), préparée à partir de minium et d'acide acétique glacial[19] et titrée potentiométriquement par une solution étalon d'hydroquinone[20].

Solution d'hydroquinone dans l'acide sulfurique à 1%, titrée par le bichromate de potassium.

Appareils

Les titrages potentiométriques ont été effectués au moyen d'un pH-mètre AK (Kovodružba, Praha), en utilisant un fil de platine comme électrode indicatrice et

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une électrode au calomel comme électrode de référence. Pour agiter le liquide, un agitateur électromagnétique a été utilisé. Les titrages ont été effectués à l'aide de microburettes de 5 ml (graduées en 0.01 ml).

RÉSULTATS

Dans nos travaux précédents, concernant la comparaison de l'effet oxydant du tétracétate de plomb ainsi que de l'acide périodique et de ses sels[12,19-22], nous avons examiné, entre autre, la possibilité d'utiliser les réactions du tétracétate de plomb en solution aqueuse et en solution dans des acides dilués, à des fins analytiques. Nous avons constaté qu'il est possible de doser, dans les conditions données, l'hydrazine et ses dérivés, par titrage potentiométrique direct, au moyen de tétracétate de plomb, de même que l'acide ascorbique[21] et quelques ions inorganiques courants (Cr^{+2}, Ti^{+3}, Fe^{+2}, Sn^{+2}, Sb^{+3}, As^{+3}).

Le dosage de l'acide tartrique par titrage potentiométrique direct[20], d'après l'équation

$$COOH\cdot CHOH\cdot CHOH\cdot COOH + 3(CH_3COO)_4Pb + 2H_2O = 2CO_2 + 2HCOOH + 3(CH_3COO)_2Pb + 6CH_3COOH \quad (1)$$

est rendu difficile par l'oxydation subséquente de l'acide formique produit. Pour cette raison, le dosage d'autres substances organiques par le tétracétate de plomb est moins favorable que, par exemple, par l'acide periodique.

Nous nous sommes efforcés par conséquent de trouver les conditions nécessaires pour obtenir une oxydation quantitative de l'acide tartrique en anhydride carbonique et eau:

$$COOH\cdot CHOH\cdot CHOH\cdot COOH + 5(CH_3COO)_4Pb + 2H_2O = 4CO_2 + 5(CH_3COO)_2Pb + 10CH_3COOH \quad (2)$$

D'après les indications de la littérature, l'oxydation de l'acide formique, ne s'effectuant que lentement en milieu d'acide acétique[23], peut être accélérée par la présence d'eau[24] et d'acétates alcalins[25]. C'est pourquoi nous avons étudié d'abord l'influence de l'eau ainsi que celle des acétates (alcalins) sur la rapidité d'oxydation de l'acide tartrique: A 10.00 ml de solution d'acide tartrique 0.005 *M* dans l'acide acétique glacial, il a été ajouté une quantité variable d'eau et d'acétate de potassium, 10.00 ml de solution de $PbAc_4$ 0.05 *M* (excédent double, comparé à l'oxydation quantitative, d'après l'équation (2)) et l'acide acétique glacial jusqu'à un volume total de 30 ml. On laisse reposer la solution pendant 10 min; la quantité de $PbAc_4$ qui n'a pas réagi est ensuite déterminée par titrage potentiométrique au moyen d'une solution d'hydroquinone 0.05 *M*. (Pendant le titrage, la solution se trouble par formation de sulfate de plomb, provenant de la réaction des ions Pb^{+2} avec l'acide sulfurique, ajouté à la solution d'hydroquinone pour augmenter sa stabilité). On effectue parallèlement un essai à blanc; la différence des volumes utilisés permet de calculer la quantité de $PbAc_4$, nécessaire à l'oxydation de l'acide tartrique. Les résultats sont donnés dans le Tableau I.

Nous avons constaté que la quantité de réactif consommée était la même après 6 h qu'après 10 min. (Milieu acide acétique à 80% + 5 g d'acétate de potassium). En effectuant l'oxydation dans des solutions plus diluées d'acide acétique (par exemple, acide acétique à 50%), il se produit une hydrolyse partielle du réactif après 20 min

TABLEAU I

OXYDATION DE L'ACIDE TARTRIQUE PAR LE TÉTRACÉTATE DE PLOMB DANS DES MILIEUX DIFFÉRENTS, APRÈS 10 MIN

Milieu	*Consommation de mols de $PbAc_4$/1 mol d'acide tartrique*
Acide acétique glacial	1.03
Acide acétique 80%	3.04
Acide acétique 80% + 0.04 g d'acétate de potassium	3.32
Acide acétique 80% + 0.4 g d'acétate de potassium	4.26
Acide acétique 80% + 1 g d'acétate de potassium	4.88
Acide acétique 80% + 5 g d'acétate de potassium	5.01

environ, ce qui n'est pas le cas avec l'acide acétique à 80%, même après un temps relativement long. Nous avons finalement ramené la quantité d'acétate de potassium à 1 g, la réaction étant alors suffisamment rapide.

Nous avons ensuite déterminé la rapidité d'oxydation de l'acide tartrique par $PbAc_4$ dans ces conditions, en ajoutant à 10.00 ml de la solution d'acide tartrique (0.005 *M* dans l'acide acétique glacial), 5 ml de la solution aqueuse d'acétate de potassium à 20% et 10.00 ml de la solution de tétracétate de plomb 0.05 *M* et en titrant après un certain temps, l'excès de réactif par la solution d'hydroquinone 0.05 *M*. Il a été effectué parallèlement un essai à blanc permettant de déterminer par différence la quantité consommée de $PbAc_4$ pour l'oxydation de l'acide tartrique. Les résultats obtenus sont donnés dans le Tableau II.

TABLEAU II

OXYDATION DE L'ACIDE TARTRIQUE PAR LE TÉTRACÉTATE DE PLOMB, EN EXCÈS, EN FONCTION DU TEMPS

Temps en min	*Consommation des mols de $PbAc_4$/1 mol d'acide tartrique*
2	3.76
5	4.40
10	4.87
20	5.00
30	5.00
45	5.02
240	4.99
360	5.00

Mode opératoire

La prise d'essai correspondante à 5 ml env. d'acide tartrique 0.01 *M* (ou la quantité correspondante du tartrate examiné) est diluée, soit: (*a*) dans 5 ml d'eau, (*b*) dans 10 ml d'acide acétique glacial, (*c*) dans 5 ml de la solution aqueuse d'acétate de potassium de 20%. On ajoute 10 ml de solution d'acétate de potassium à 10% dans l'acide acétique glacial (*a*), ou 5 ml de la solution aqueuse d'acétate de potassium à 20% (*b*), ou 10 ml d'acide acétique glacial (*c*). Finalement, on ajoute 10.00 ml de la solution de $PbAc_4$ 0.05 *M*. Après 30 min, la quantité de $PbAc_4$ non consommée est déterminée par titrage potentiométrique au moyen d'une solution d'hydroquinone

0.05 *M*. On exécute parallèlement un essai à blanc et, de la différence des quantités consommées, on peut calculer la teneur de la substance à doser.

1 ml de $PbAc_4$ 0.05 *M* (= 1 ml d'hydroquinone 0.05 *M*) correspond à 1.5009 mg d'acide tartrique. La différence décisive de la méthode est de 0.18%.

On a pu ainsi déterminer la teneur en tartrate des composés suivants: $KNaC_4H_4O_6 \cdot 4H_2O$, $KC_4H_5O_6$, $Na_5Bi(C_4H_2O_6)_2 \cdot 9H_2O$, $Na_5Bi(C_4H_2O_6)_2 \cdot 6H_2O$, $K_5Bi(C_4H_2O_6)_2 \cdot 4H_2O$, $LiBi(C_4H_2O_6)_2 \cdot 8H_2O$ et $BiC_8H_9O_{12}$. Tous ces tartrates sont facilement solubles dans l'eau, excepté $BiC_8H_9O_{12}$, qu'on peut dissoudre à chaud dans une solution d'acétate de potassium à 20%.

RÉSUMÉ

En milieu d'acide acétique à 80%, en présence d'acétate de potassium, l'oxydation de l'acide tartrique par le tétracétate de plomb s'effectue quantitativement. Lors du dosage volumétrique indirect de l'acide tartrique et des tartrates, on ajoute un excès de $PbAc_4$; après 30 min, cet excès est déterminé par titrage potentiométrique à l'aide d'une solution d'hydroquinone.

SUMMARY

It was found, that in a medium of 80% acetic acid, in the presence of potassium acetate the oxidation of tartaric acid by lead(IV)-acetate takes place quantitatively. In the indirect determination of tartaric acid and tartrates, an excess of lead(IV)-acetate is used, allowing 30 min for the reaction to take place. The remaining reagent is then determined by potentiometric titration with a volumetric hydroquinone solution.

ZUSAMMENFASSUNG

Beschreibung einer indirekten Methode zur Bestimmung von Weinsäure und Tartraten durch Oxydation mit Blei-(IV)-acetat. Der Überschuss an Blei-(IV)-acetat wird mit einer Hydrochinonlösung potentiometrisch titriert. Der quantitative Verlauf der Oxydation wird nachgewiesen.

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METHOD FOR DETERMINATION OF THE EQUIVALENCE POINT IN POTENTIOMETRIC TITRATIONS

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INTRODUCTION

In the literature a number of methods are described for determination of the equivalence point in potentiometric titrations. It is clear that if the equivalence point and the inflection point of the potential–volume curve coincide, the end-point is reached when the second derivative is zero.

KOLTHOFF[1-3] and other authors[4-6], however, regard the zero value of the second difference as the end-point of the titration. This may lead to inaccurate results, as has been shown by HAHN[7-9].

In addition several methods of graphical determination of the inflection point have been proposed in the literature, *e.g.* TUBBS' concentric-arcs method[10], which has no theoretical basis, GRAN's method[11] of transformed titration curves and the method of "equal areas" described by KOHN AND ZITKO[12]. These methods require a graphical representation of the experimental results and a visual evaluation of the end-point.

HAHN[9] published a method of calculation which yields accurate results but its application is limited.

We have developed an accurate method which can be applied more generally to symmetric potentiometric titrations when a graph as shown in Fig. 7 is available. Our method is simple, requires no graphical representation of the experimental results and possesses a theoretical basis. In addition it gives approximate values for the ionization constant of the slightly dissociated substance formed during the titration. The theory of the method is outlined below.

THEORY

The equation of a symmetric potential–volume curve will be derived and the differences between potentials corresponding to equidistant volumes near the end-point will be calculated. Further it will be shown that ratios between the differences mentioned are functions of two parameters which determine the end-point and the ionization constant respectively.

In addition, the influence of dilution on the two parameters will be studied.

List of symbols used

Symbol	*Meaning*	*Dimension*
K	ionization constant	$mmol^2 ml^{-2}$
[A]	concentration of A	$mmol\ ml^{-1}$
t	titre of the reagent	$mmol\ ml^{-1}$
v	volume of the reagent added	ml
V	initial volume of the solution to be titrated	ml
v_0	volume of the reagent added at the equivalence point	ml
pA	$-\log$ A	—
pK	$-\log K$	—
e	base of natural system of logarithms	—
E	electromotive force of a cell	mV
E_0	electromotive force with [A] = 1 mmol/ml	mV
F	Faraday constant (96,500)	$C\ mol^{-1}$
α	constant	mV
β	constant ($= RT/F$)	mV
R	gas constant (= 8.315)	$mV\ C\ deg^{-1} mol^{-1}$
T	absolute temperature	deg
$\varrho, \varrho_a, \varrho_b$	parameters determining the equivalence point	—
$\varrho_K, \varrho_H, \varrho_F$	ϱ-values found by Kolthoff's, Hahn's and our method respectively	—
$\varkappa, \varkappa_a, \varkappa_b$	parameters determining the ionization constant ($\varkappa = \sqrt{K/t\varphi}$)	—
$\varphi, \varphi_a, \varphi_b$	parameters determining the dilution ($\varphi = \Delta v/V_e$)	—
$\tau_0\tau_1\tau_2\tau_3$	potential steps of fixed order	mV
$\Delta_0\Delta_1\Delta_2\Delta_3$	potential steps of decreasing order	mV
Δv	volumes added during the titration	ml
$E_aE_bE_c$	potentials between the steps τ_0 and τ_1	mV
$v_av_bv_c$	volumes added at the potentials $E_aE_bE_c$ respectively	ml
$V_aV_bV_c$	volumes of the solution being titrated at the potentials E_a, E_b and E_c respectively	ml
j, n	integers	—
Z	function of the parameters ϱ, $\varkappa$ and φ	—
$r_1r_2r_3$	ratios of potential steps of fixed order ($r_j = \tau_j/\tau_{j-1}$)	—
$R_1R_2R_3$	ratios of potential steps of decreasing order ($R_j = \Delta_j/\Delta_{j-1}$)	—

Derivation of a general expression for the potentiometric titration curve of the system $A + D \rightarrow AD$

If a strong electrolyte AB is titrated with another strong electrolyte CD to form a slightly dissociated substance AD with an ionization constant K, the following equations apply:

$$[A]\cdot[D] = K \tag{1}$$

$$[B] = \frac{tv_0}{V + v} \tag{2}$$

$$[C] = \frac{tv}{V + v} \tag{3}$$

and

$$[A] + [C] = [B] + [D] \tag{4}$$

These equations yield:

$$\frac{\sqrt{K}}{[A]} - \frac{[A]}{\sqrt{K}} = \frac{t(v - v_0)}{\sqrt{K}(V + v)} \tag{5}$$

With

$$pA = -\log [A] \tag{6}$$

and

$$pK = -\log K \tag{7}$$

it follows that:

$$\frac{\sqrt{K}}{[A]} - \frac{[A]}{\sqrt{K}} = \exp\left\{\ln \frac{\sqrt{K}}{[A]}\right\} - \exp\left\{-\ln \frac{\sqrt{K}}{[A]}\right\} = 2 \sinh\left(\frac{pA - \frac{1}{2}pK}{\log e}\right) \tag{8}$$

Combination of (5) and (8) and resolution of the equation for pA, gives

$$pA = \tfrac{1}{2}pK + (\log e) \sinh^{-1} \frac{t(v - v_0)}{2\sqrt{K}(V + v)} \tag{9}*$$

The electromotive force of a cell can be calculated from

$$E = E_0 - \frac{RT}{F} \ln [A] \tag{10}$$

Substitution of (6) in (10) gives

$$E = E_0 + \frac{RT}{F \log e} pA \tag{11}$$

Substitution of (9) in (11) gives

$$E = E_0 + \frac{RT}{2F \log e} pK + \frac{RT}{F} \sinh^{-1}\left\{\frac{t(v - v_0)}{2\sqrt{K}(V + v)}\right\} \tag{12}$$

This formula can be considered as the general equation of the potential–volume curve of the system mentioned above.

At the temperature T the values:

$$\alpha = E_0 + \frac{RT}{2F \log e} pK \qquad \text{and} \qquad \beta = \frac{RT}{F} \tag{13}$$

* $y = \sinh^{-1} x$, if $x = \sinh y = (e^y - e^{-y})/2$.

are constants. Consequently,

$$E = \alpha + \beta \sinh^{-1} \frac{t(v - v_0)}{2\sqrt{K(V + v)}} \tag{14}$$

and after the j-th addition:

$$E_j = \alpha + \beta Z_j \tag{15}$$

where

$$Z_j = \sinh^{-1} \frac{t(v_j - v_0)}{2\sqrt{K(V + v_j)}} \tag{16}$$

Determination of the equivalence point

Case a

A titration curve of the type represented in Fig. 1a can be obtained when a solution is titrated with equal increments Δv of a reagent. The volume v_a corresponds to the potential E_a between the steps τ_1 and τ_0. The volume v_0 at the equivalence point is determined by the equation:

$$v_0 = v_a + \varrho_a \Delta v \tag{17a}$$

Consequently, v_0 can be calculated if ϱ_a is known. In the next section a method will be developed for obtaining ϱ_a-values ($0 \leqslant \varrho_a \leqslant 0.50$).

Case b

A titration curve of the type represented in Fig. 1b can be obtained when a solution is titrated with equal increments Δv of a reagent. The volume v_b corresponds to the potential E_b between the steps τ_0 and τ_1. The volume v_0 at the equivalence point is determined by the equation:

$$v_0 = v_b - \varrho_b \Delta v \tag{17b}$$

Consequently, v_0 can be calculated if ϱ_b is known. In the next section a method will be developed for obtaining ϱ_b-values ($0 \leqslant \varrho_b \leqslant 0.50$).

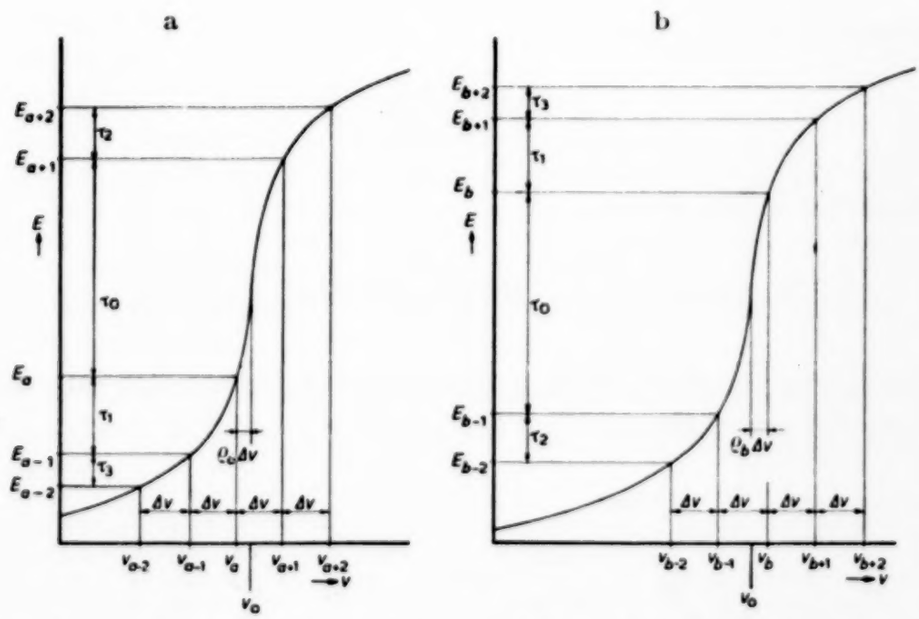

Fig. 1. Symmetric potential–volume curves (effect of dilution neglected; $\varphi = 0$).

Determination of the parameters ϱ and $\varkappa$

The ratios of potential steps are independent of α and β (see eqn. 14). Defining the ratio r_j of the potential steps τ_j and τ_{j-1} as:

$$r_j = \frac{\tau_j}{\tau_{j-1}}$$

we get:

from Fig. 1a and eqn. (15):

$$\left.\begin{aligned} r_1 &= \frac{\tau_1}{\tau_0} = \frac{Z_a - Z_{a-1}}{Z_{a+1} - Z_a} \\ r_2 &= \frac{\tau_2}{\tau_1} = \frac{Z_{a+2} - Z_{a+1}}{Z_a - Z_{a-1}} \\ r_3 &= \frac{\tau_3}{\tau_2} = \frac{Z_{a-1} - Z_{a-2}}{Z_{a+2} - Z_{a+1}} \end{aligned}\right\} \quad (18a)$$

With:

$$\left.\begin{aligned} v_j &= j \cdot \Delta v \\ v_a &= a \cdot \Delta v \end{aligned}\right\} \quad (19a)$$

$$\left.\begin{aligned} V_a &= V + v_a \\ \varphi_a &= \frac{\Delta v}{V_a} \\ \varkappa_a &= \frac{\sqrt{K}}{t\varphi_a} \end{aligned}\right\} \quad (20a)$$

it follows from eqns. (16) and (17a) that:

$$Z_{a+n} = \sinh^{-1}\left\{\frac{(n - \varrho_a)}{2\varkappa_a(1 + n\varphi_a)}\right\} \quad (21a)$$

from Fig. 1b and eqn. (15):

$$\left.\begin{aligned} r_1 &= \frac{\tau_1}{\tau_0} = \frac{Z_{b+1} - Z_b}{Z_b - Z_{b-1}} \\ r_2 &= \frac{\tau_2}{\tau_1} = \frac{Z_{b-1} - Z_{b-2}}{Z_{b+1} - Z_b} \\ r_3 &= \frac{\tau_3}{\tau_2} = \frac{Z_{b+2} - Z_{b+1}}{Z_{b-1} - Z_{b-2}} \end{aligned}\right\} \quad (18b)$$

With:

$$\left.\begin{aligned} v_j &= j \cdot \Delta v \\ v_b &= b \cdot \Delta v \end{aligned}\right\} \quad (19b)$$

$$\left.\begin{aligned} V_b &= V + v_b \\ \varphi_b &= \frac{\Delta v}{V_b} \\ \varkappa_b &= \frac{\sqrt{K}}{t\varphi_b} \end{aligned}\right\} \quad (20b)$$

it follows from eqns. (16) and (17b) that:

$$Z_{b+n} = \sinh^{-1}\left\{\frac{(n + \varrho_b)}{2\varkappa_b(1 + n\varphi_b)}\right\} \quad (21b)$$

Substitution of (21a) in (18a) gives the equations

$$\left.\begin{aligned} r_1 &= \frac{\sinh^{-1}\left\{\frac{1 + \varrho_a}{2\varkappa_a(1 - \varphi_a)}\right\} - \sinh^{-1}\left\{\frac{\varrho_a}{2\varkappa_a}\right\}}{\sinh^{-1}\left\{\frac{1 - \varrho_a}{2\varkappa_a(1 + \varphi_a)}\right\} + \sinh^{-1}\left\{\frac{\varrho_a}{2\varkappa_a}\right\}} \\ r_2 &= \frac{\sinh^{-1}\frac{2 - \varrho_a}{2\varkappa_a(1 + 2\varphi_a)} - \sinh^{-1}\frac{1 - \varrho_a}{2\varkappa_a(1 + \varphi_a)}}{\sinh^{-1}\left\{\frac{1 + \varrho_a}{2\varkappa_a(1 - \varphi_a)}\right\} - \sinh^{-1}\left\{\frac{\varrho_a}{2\varkappa_a}\right\}} \\ r_3 &= \frac{\sinh^{-1}\left\{\frac{2 + \varrho_a}{2\varkappa_a(1 - 2\varphi_a)}\right\} - \sinh^{-1}\left\{\frac{1 + \varrho_a}{2\varkappa_a(1 - \varphi_a)}\right\}}{\sinh^{-1}\left\{\frac{2 - \varrho_a}{2\varkappa_a(1 + 2\varphi_a)}\right\} - \sinh^{-1}\left\{\frac{1 - \varrho_a}{2\varkappa_a(1 + \varphi_a)}\right\}} \end{aligned}\right\} \quad (22a)$$

Substitution of (21b) in (18b) gives the equations

$$\left.\begin{aligned} r_1 &= \frac{\sinh^{-1}\left\{\frac{1+\varrho_b}{2\varkappa_b(1+\varphi_b)}\right\} - \sinh^{-1}\left\{\frac{\varrho_b}{2\varkappa_b}\right\}}{\sinh^{-1}\left\{\frac{1-\varrho_b}{2\varkappa_b(1-\varphi_b)}\right\} + \sinh^{-1}\left\{\frac{\varrho_b}{2\varkappa_b}\right\}} \\ r_2 &= \frac{\sinh^{-1}\left\{\frac{2-\varrho_b}{2\varkappa_b(1-2\varphi_b)}\right\} - \sinh^{-1}\left\{\frac{1-\varrho_b}{2\varkappa_b(1-\varphi_b)}\right\}}{\sinh^{-1}\left\{\frac{1+\varrho_b}{2\varkappa_b(1+\varphi_b)}\right\} - \sinh^{-1}\left\{\frac{\varrho_b}{2\varkappa_b}\right\}} \\ r_3 &= \frac{\sinh^{-1}\left\{\frac{2+\varrho_b}{2\varkappa_b(1+2\varphi_b)}\right\} - \sinh^{-1}\left\{\frac{1+\varrho_b}{2\varkappa_b(1+\varphi_b)}\right\}}{\sinh^{-1}\left\{\frac{2-\varrho_b}{2\varkappa_b(1-2\varphi_b)}\right\} - \sinh^{-1}\left\{\frac{1-\varrho_b}{2\varkappa_b(1-\varphi_b)}\right\}} \end{aligned}\right\} \quad (22b)$$

With $\varphi_a \approx 0$ and $\varphi_b \approx 0$, eqns. (22a) and (22b) both yield:

$$\left.\begin{aligned} r_1 &= \frac{\sinh^{-1}\left(\frac{1+\varrho}{2\varkappa}\right) - \sinh^{-1}\left(\frac{\varrho}{2\varkappa}\right)}{\sinh^{-1}\left(\frac{1-\varrho}{2\varkappa}\right) + \sinh^{-1}\left(\frac{\varrho}{2\varkappa}\right)} \\ r_2 &= \frac{\sinh^{-1}\left(\frac{2-\varrho}{2\varkappa}\right) - \sinh^{-1}\left(\frac{1-\varrho}{2\varkappa}\right)}{\sinh^{-1}\left(\frac{1+\varrho}{2\varkappa}\right) - \sinh^{-1}\left(\frac{\varrho}{2\varkappa}\right)} \\ r_3 &= \frac{\sinh^{-1}\left(\frac{2+\varrho}{2\varkappa}\right) - \sinh^{-1}\left(\frac{1+\varrho}{2\varkappa}\right)}{\sinh^{-1}\left(\frac{2-\varrho}{2\varkappa}\right) - \sinh^{-1}\left(\frac{1-\varrho}{2\varkappa}\right)} \end{aligned}\right\} \quad (23)$$

where $\varrho = \varrho_a = \varrho_b$ and $\varkappa = \varkappa_a = \varkappa_b$. Further we define:

$$\varkappa = \frac{\sqrt{K}}{t\varphi} \quad \text{and} \quad \varphi = \frac{\Delta v}{V_e}$$

where V_e is the volume of the solution corresponding to the potential between τ_0 and τ_1 Values of r_1, r_2 and r_3 have been calculated after substitution of a number of ϱ- and $\varkappa$-values in the eqns. (23). The results are represented in Fig. 2. Here the ratios r_1 and r_3 are plotted against the ratio r_2 and curves are drawn through points referring to equal ϱ- and equal $\varkappa$-values respectively. When r_2 and r_1 or r_3 are known the ϱ- and $\varkappa$-value of a symmetric potentiometric titration can be read from Fig. 2. (More details are given in Fig. 7.) Fig. 2 shows that low $\varkappa$-values (*e.g.* $\varkappa < 0.15$) found from r_1 and r_2 are more accurate than those found from r_2 and r_3. Therefore we recommend the determination of the $\varkappa$-values from r_1 and r_2.

Influence of dilution

Effect of $\varphi \neq 0$ on ϱ. When $\varphi \neq 0$, eqns. (22a) and (22b) must be used. After substitution of $\varphi = 0.01$ and different values of ϱ_a, $\varkappa_a$, ϱ_b and $\varkappa_b$, the ratios r_1, r_2 and r_3 have been calculated by means of these formulae. The results are represented in Fig. 3

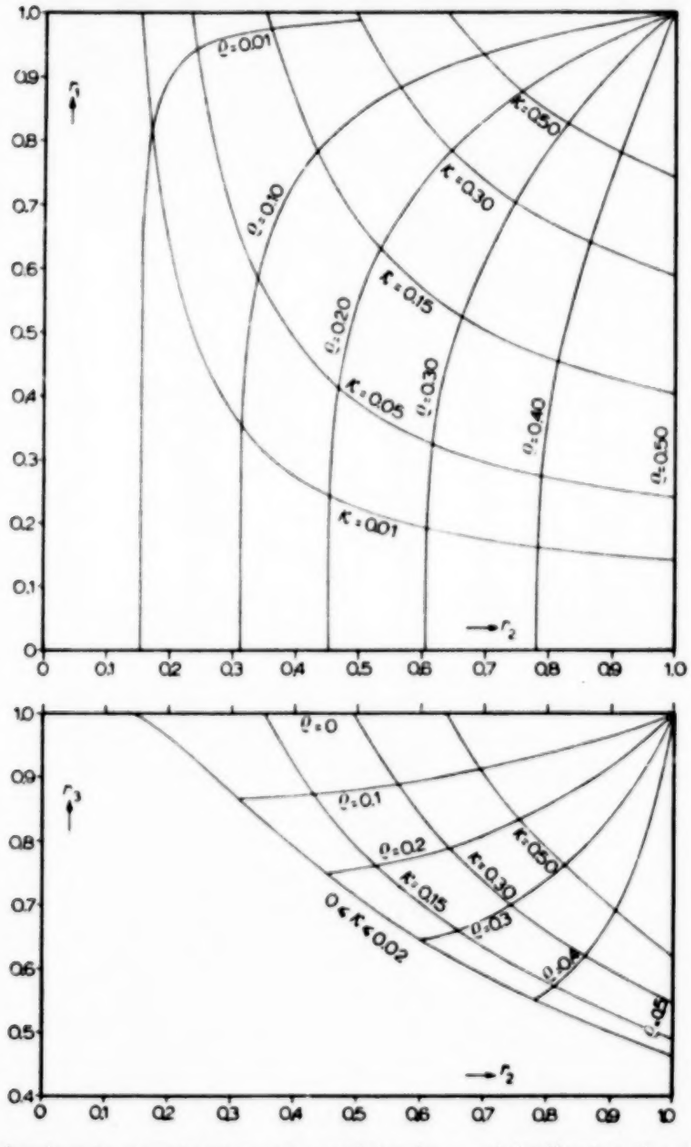

Fig. 2. Each curve referring to constant ϱ- or $\varkappa$-values ($\varphi = 0$) indicates the relationship between the ratios r_2 and r_1 or r_3. The data have been calculated with eqn. (23).

where lines are drawn through points referring to equal ϱ_a- and ϱ_b-values. The ϱ_a- and ϱ_b-curves correspond to values calculated with eqns. (22a) and (22b) respectively. The dashed ϱ-curves obtained from the eqns. (23), refer to $\varphi = 0$ and correspond to the ϱ-curves in Fig. 2. Fig. 3 shows that the ϱ-values derived from r_2 and r_3 are more influenced by $\varphi \neq 0$ than the ϱ-values derived from r_1 and r_2. A deviation $\Delta\varrho \leqslant 0.015$ ($\Delta\varrho \leqslant 0.025$) of the ϱ-value derived from r_1 and r_2 (r_2 and r_3) can be expected if $\varkappa \leqslant 0.3$ and the influence of $\varphi \leqslant 0.01$ is neglected. Generally, the value $\Delta\varrho \leqslant 0.015$ is small in proportion to the deviation in ϱ caused by errors in the experimentally determined ratios of potential steps. Therefore we recommend the determination of the ϱ-values from r_1 and r_2 and the neglect of the effect of $\varphi \leqslant 0.01$ if $\varkappa \leqslant 0.3$.

Effect of $\varphi \neq 0$ on $\varkappa$. After substitution of $\varphi = 0.01$ and different values of ϱ_a, $\varkappa_a$, ϱ_b and $\varkappa_b$ in eqns. (22a) and (22b), the ratios r_1, r_2 and r_3 have been calculated. The results are represented in Fig. 4, where lines are drawn through points referring to equal $\varkappa_a$ and $\varkappa_b$ values. The curves marked $\varkappa_a$ and $\varkappa_b$ correspond to

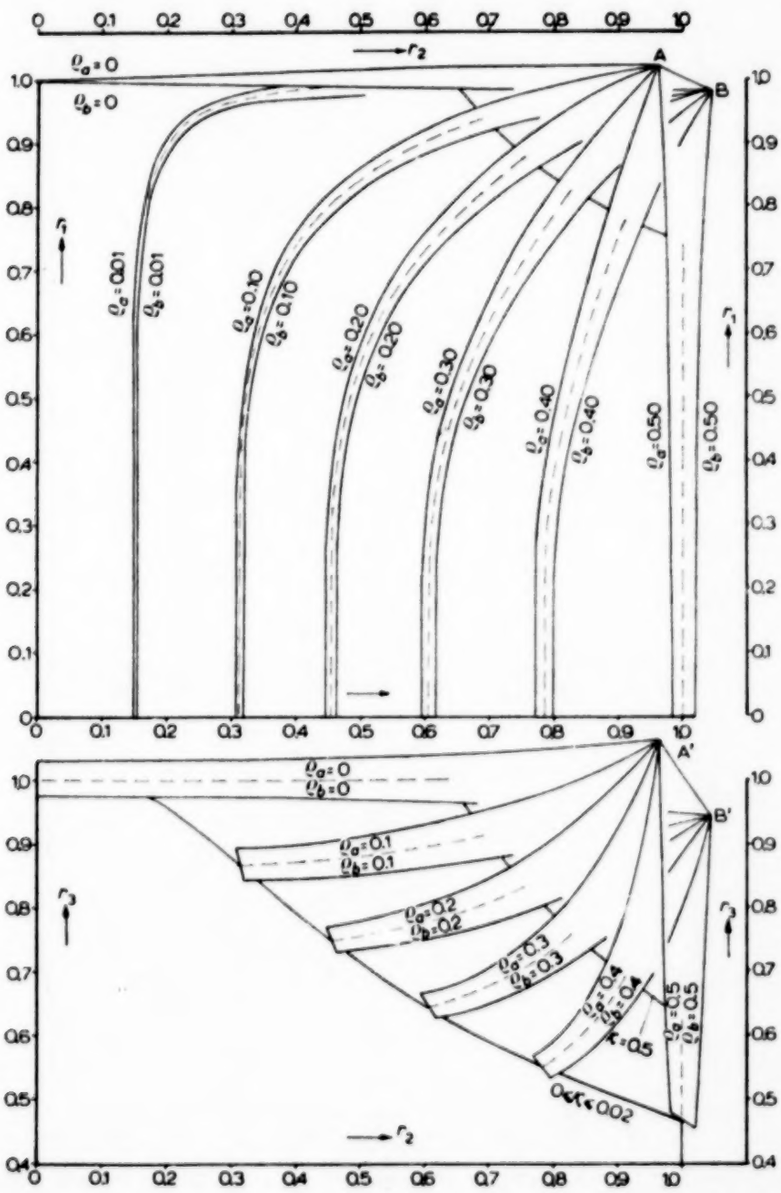

Fig. 3. The full lines ($\varphi_a = 0.01 = \varphi_b$) refer to eqns. (22a) and (22b); the dashed curves ($\varphi = 0$) to the eqns. (23).

values found from eqns. (22a) and (22b) respectively. Each $\varkappa$-curve represented in Fig. 2 and referring to $\varphi = 0$, lies between the corresponding $\varkappa_a$- and $\varkappa_b$-curves of Fig. 4. Fig. 4 shows that the influence of $\varphi \neq 0$ on the $\varkappa$-values derived from r_1 and r_2 is smaller than the effect of $\varphi \neq 0$ on the $\varkappa$-values from r_2 and r_3. Consequently, if the influence of $\varphi \neq 0$ is neglected $\varkappa$-values derived from r_1 and r_2 are to be preferred. In the next section it will be shown that if $\varkappa \leqslant 0.5$ and the influence of $\varphi \leqslant 0.05$ is neglected the errors in the ratios of the potential steps found from experimental data determine the accuracy of $\varkappa$.

Introduction of potential steps of decreasing order. If a solution is titrated with equal

increments Δv of the reagent and Δ_0, Δ_1 and Δ_2 are potential steps of decreasing order, the ratios:

$$R_1 = \frac{\Delta_1}{\Delta_0} \quad \text{and} \quad R_2 = \frac{\Delta_2}{\Delta_1}$$

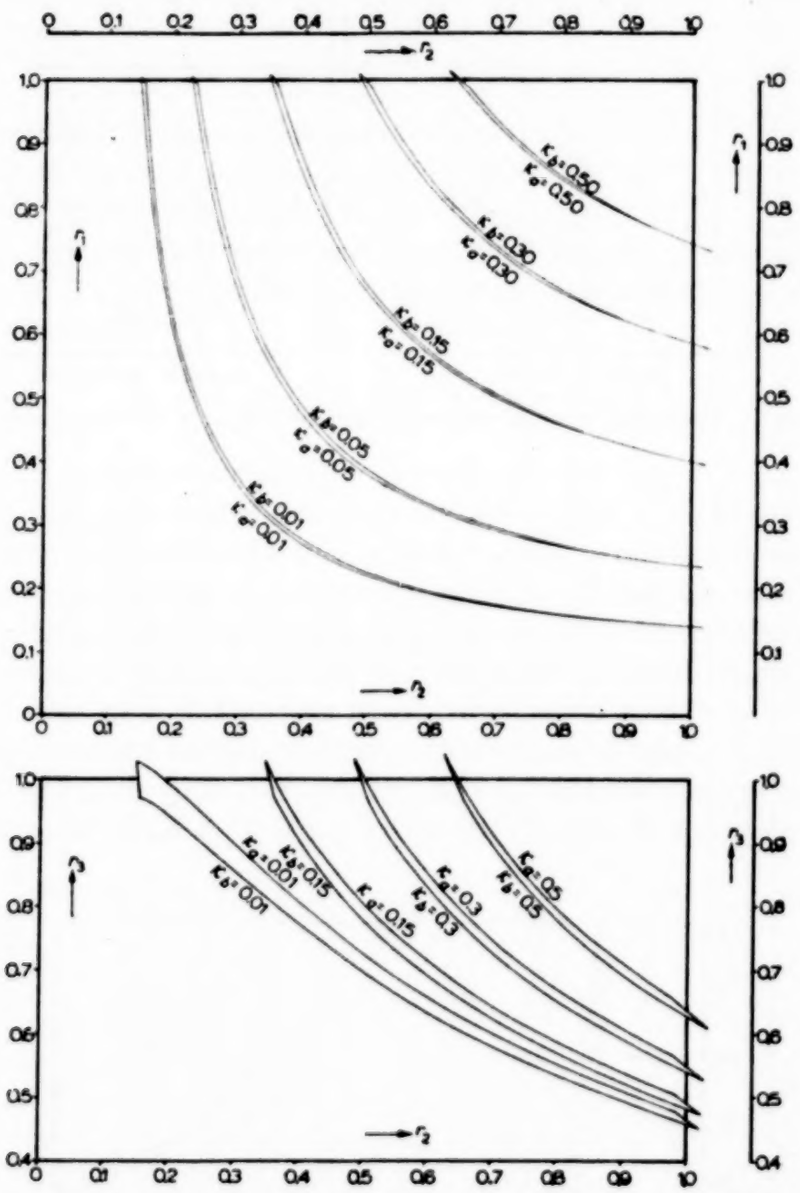

Fig. 4. The curves refer to data calculated with eqns. (22a) and (22b) after substitution of $\varphi_a = 0.01 = \varphi_b$.

cannot exceed the value 1. From Fig. 1 it can be seen that generally:

$$R_1 = \frac{\Delta_1}{\Delta_0} = \frac{\tau_1}{\tau_0} = r_1 \quad \text{and} \quad R_2 = \frac{\Delta_2}{\Delta_1} = \frac{\tau_2}{\tau_1} = r_2 \tag{24}$$

If, however, $\varphi \neq 0$ the ratios r_1 and r_2 may occasionally exceed the value 1. With $r_1 > 1$ (see points near $\varrho_a = 0$ in Fig. 3) and $r_2 > 1$ (see points near $\varrho_b = 0.5$ in Fig. 3) the eqns. (24) are not applicable. With $r_1 > 1$ (see Fig. 5a) it appears that:

$$R_1 = \frac{\Delta_1}{\Delta_0} = \frac{\tau_0}{\tau_1} = \frac{1}{r_1} \quad \text{and} \quad R_2 = \frac{\Delta_2}{\Delta_1} = \frac{\tau_3}{\tau_0} = r_1 r_2 r_3 \tag{25a}$$

With $r_2 > 1$ (see Fig. 5b) we get:

$$R_1 = \frac{\Delta_1}{\Delta_0} = \frac{\tau_2}{\tau_0} = r_1 r_2 \quad \text{and} \quad R_2 = \frac{\Delta_2}{\Delta_1} = \frac{\tau_1}{\tau_2} = \frac{1}{r_2} \tag{25b}$$

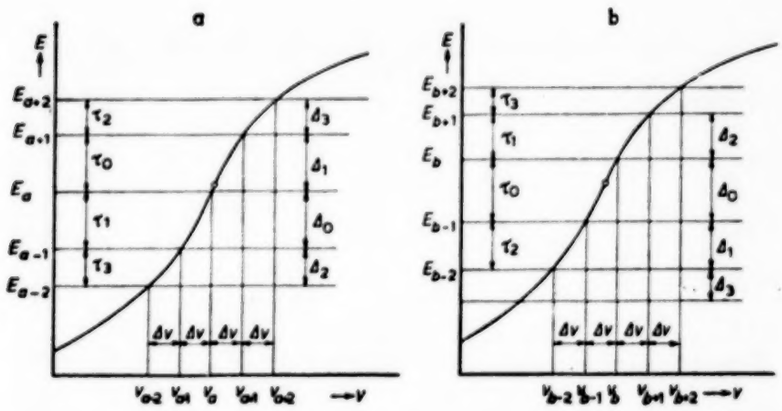

Fig. 5. Potential volume curves (effect of dilution not neglected).

After substitution of $\varphi_a = 0.05 = \varphi_b$ and different values of ϱ_a, $\varkappa_a$, ϱ_b and $\varkappa_b$ in the eqns. (22) we calculated the ratios r_1, r_2 and r_3. Substitution of the results in eqns. (24) and (25) leads to the R_1- and R_2-values plotted in Fig. 6. In this figure curves have been drawn through points with equal $\varkappa_a$- and $\varkappa_b$-values. The dashed $\varkappa$-lines which refer to $\varphi = 0$, have been obtained by the eqns. (23) and correspond to $\varkappa$-lines in Fig. 2.

If the effect of $\varphi \leqslant 0.05$ is neglected, each pair of full lines shows the maximum deviations of the $\varkappa$-values from the corresponding dashed curves. Fig. 6 shows that these deviations are smaller than the deviations caused by errors in the experimentally determined ratios R_1 and R_2 (the errors in R_1 and R_2 do not exceed 5% if the

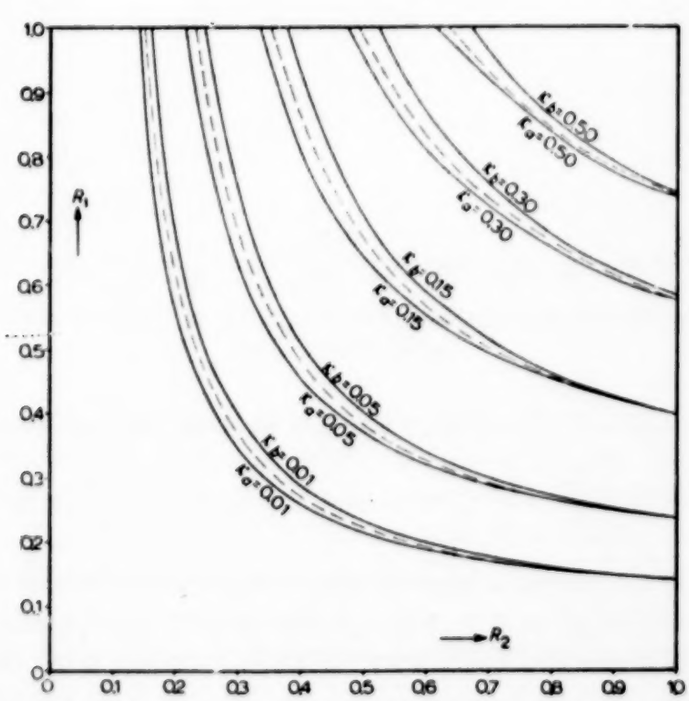

Fig. 6. The full lines ($\varphi_a = 0.05 = \varphi_b$) refer to data calculated with (22), (24) and (25); the dashed lines ($\varphi = 0$) to data derived from eqns. (23) and (24).

experimental conditions are favourable). Consequently, the effect of $\varphi \leqslant 0.05$ on $\varkappa$ may be neglected if $\varkappa \leqslant 0.5$.

PROCEDURE

The method can be applied to potentiometric titrations of the type:

$$A + D \rightarrow AD$$

The procedure can be summarized as follows:

(*a*) Take V ml of the solution containing the substance A.

(*b*) Titrate with equal portions Δv ($\leqslant 0.01\ V$) of D, titre t.

(*c*) Determine the potential steps in decreasing order Δ_0, Δ_1 and Δ_2 and the added volume v_e, which corresponds with the potential between Δ_0 and Δ_1.

(*d*) Calculate the ratios

$$R_1 = \Delta_1/\Delta_0,\ R_2 = \Delta_2/\Delta_1 \text{ and } \varphi = \Delta v/(V + v_e). \tag{26}$$

(*e*) Determine the parameters ϱ and $\varkappa$ from R_1, R_2 and Fig. 7.

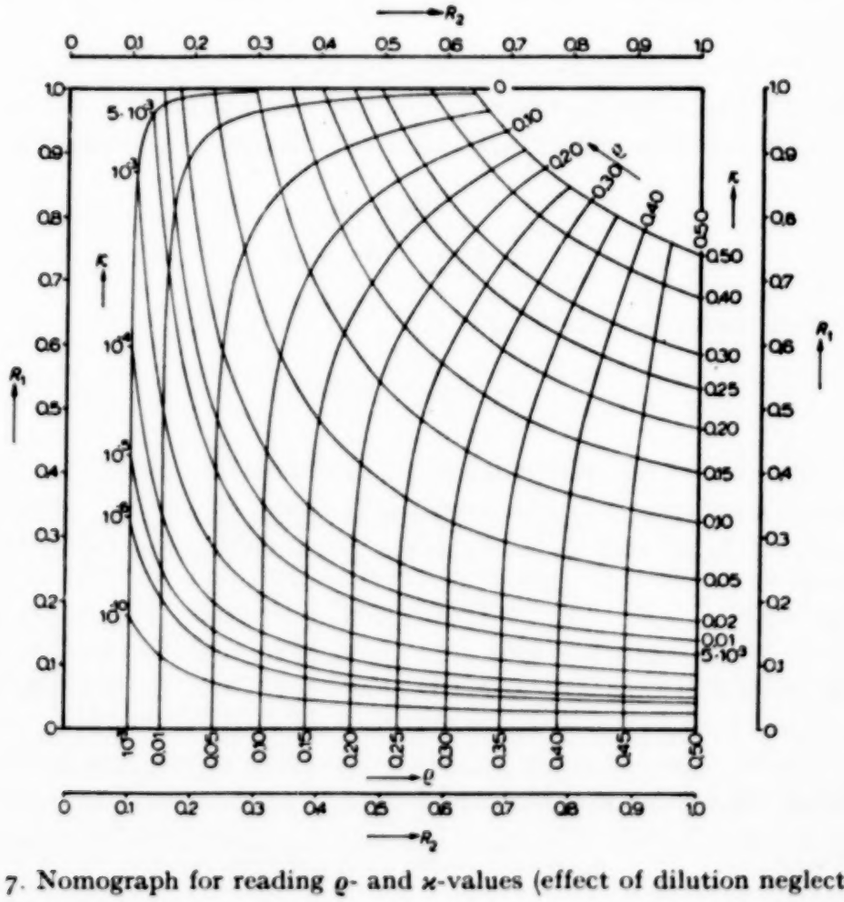

Fig. 7. Nomograph for reading ϱ- and $\varkappa$-values (effect of dilution neglected).

(*f*) Calculate the equivalence amount v_0 from:

$$\begin{aligned} v_0 &= v_e + \varrho\Delta v \text{ (27a) if } \Delta_1 \text{ precedes } \Delta_0\text{; or} \\ v_0 &= v_e - \varrho\Delta v \text{ (27b) if } \Delta_0 \text{ precedes } \Delta_1. \end{aligned} \tag{27}$$

With $\varphi \leqslant 0.01$ and $\varkappa \leqslant 0.3$ the accuracy of ϱ is determined by the errors in R_1 and R_2.

(*g*) Calculate the ionization constant from:

$$K = (t\varphi\varkappa)^2 \tag{28}$$

With $\varphi \leqslant 0.05$ and $\varkappa \leqslant 0.5$ the accuracy of $\varkappa$ is determined by the errors in R_1 and R_2.

(*f*) The limits of the applicability of the method are:

$$\frac{\sqrt{K}}{t} \leqslant 3 \cdot 10^{-3} \text{ if } \varrho \text{ is to be determined, and} \tag{29a}$$

$$\frac{\sqrt{K}}{t} \leqslant 25 \cdot 10^{-3} \text{ if } \varkappa \text{ is to be determined.} \tag{29b}$$

DISCUSSION OF VARIOUS CALCULATION METHODS

Procedures

The procedures of two other methods will be summarized. They are applied after potentiometric titration of a solution carried out by addition of constant increments Δv of the reagent.

(*a*) KOLTHOFF[1-3] recommends determination of the largest potential step Δ_0, steps Δ_b and Δ_a before and after Δ_0 respectively and the volume v_K, which corresponds with the potential between Δ_b and Δ_0. After calculation of the parameter:

$$\varrho_K = \frac{\Delta_0 - \Delta_b}{2\,\Delta_0 - (\Delta_a + \Delta_b)} \tag{30}$$

the equivalence amount v_0 is derived from

$$v_0 = v_K + \varrho_K \Delta v \tag{31}$$

(*b*) HAHN[9] determines the potential steps in decreasing order Δ_0, Δ_1, Δ_2 and the volume v_c, which corresponds to the potential between Δ_0 and Δ_1. After calculation of $R_1 = \Delta_1/\Delta_0$, $R_2 = \Delta_2/\Delta_1$ and $R_3 = \Delta_3/\Delta_2$ the parameter ϱ_H is found from:

$$\left.\begin{array}{lll} (i) & \varrho_H = \tfrac{1}{2}R_2 & \text{if } R_1 \leqslant \tfrac{1}{2}R_2 \text{ and } 0.30 \leqslant \tfrac{1}{2}R_2 \leqslant 0.50 \\ (ii) & \varrho_H = \tfrac{1}{2}R_2 - 0.35(0.3 - \tfrac{1}{2}R_2) & \text{if } R_1 \leqslant \tfrac{1}{2}R_2 \text{ and } 0.15 < \tfrac{1}{2}R_2 < 0.30 \\ (iii) & \varrho_H = -1.58 \log R_3 & \text{if } R_1 \leqslant \tfrac{1}{2}R_2 \text{ and } 0 \leqslant \tfrac{1}{2}R_2 \leqslant 0.15 \\ & & \text{or if } R_1 > \tfrac{1}{2}R_2 \end{array}\right\} \tag{32}$$

The equivalence amount v_0 is calculated from:

$$\begin{gathered} v_0 = v_c + \varrho_H \Delta v, \text{ if } \Delta_1 \text{ precedes } \Delta_0 \\ \text{or } v_0 = v_c - \varrho_H \Delta v, \text{ if } \Delta_0 \text{ precedes } \Delta_1 \end{gathered} \tag{33}$$

(*c*) The ϱ-value found by our method will be indicated with the symbol ϱ_F. In the next section the values of ϱ_K, ϱ_H and ϱ_F will be compared to the neglect of the effect of dilution.

Comparison of the methods

If $\Delta_b > \Delta_a$, we obtain $\Delta_b = \Delta_1$ and $\Delta_a = \Delta_2$. Substitution of these data and eqn. (24) in (30) gives

$$\varrho_K = 0.5 - \frac{0.5\, R_1(1 - R_2)}{2 - R_1(1 + R_2)} \tag{34a}$$

If $\Delta_b < \Delta_a$, we obtain $\Delta_b = \Delta_2$ and $\Delta_a = \Delta_1$. Substitution of these data and eqn. (24) in (30) gives

$$\varrho_K = 0.5 + \frac{0.5\, R_1(1 - R_2)}{2 - R_1(1 + R_2)} \tag{34b}$$

After substitution of different ϱ- and $\varkappa$-values in the eqns. (23), the ratios R_1 ($= r_1$), R_2 ($= r_2$) and R_3 ($= r_3$) have been calculated. Substitution of these ratios in eqns. (32) and (34) and application of the procedures described above, give the values of ϱ_K, ϱ_H and ϱ_F. These data have been plotted against the true ϱ-value in Figs. 8 and 9.

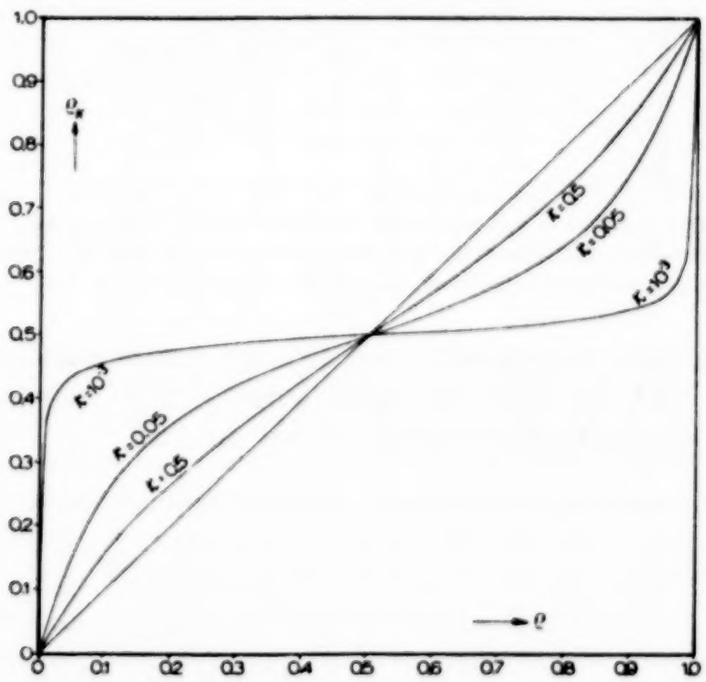

Fig. 8. Comparison between the ϱ_K-values found by Kolthoff's method and the true ϱ-values (effect of dilution neglected).

Fig. 8 shows that large deviations occur between ϱ_K and ϱ. These deviations increase with decreasing $\varkappa$-values. With $\varkappa < 10^{-3}$, $\varrho_K \approx 0.5$ is found for nearly all ϱ-values. As a result, systematic errors will be introduced when the equivalence point is determined by interpolation with ϱ_K-values. Fig. 9 shows that the deviations between ϱ_H and ϱ decrease with decreasing $\varkappa$-values; ϱ_H and ϱ are equal when $0 < \varkappa < 0.10$.

We have already pointed out that ϱ_F and ϱ are equal at all $\varkappa$-values.

Influence of $\varkappa$ on the potential–volume curve

If the effect of dilution is neglected ($\varphi_a = 0$) and $Z_{a+n} = Z$ eqn. (21a) leads to:

$$Z = \sinh^{-1}\left(\frac{n - \varrho}{2\varkappa}\right) \tag{35}$$

In Fig. 10 the values of Z (proportional to the potential E) obtained from eqn. (35) have been plotted against n (proportional to the volume v). The influence of $\varkappa$ on the type of the titration curve becomes clear from Fig. 10.

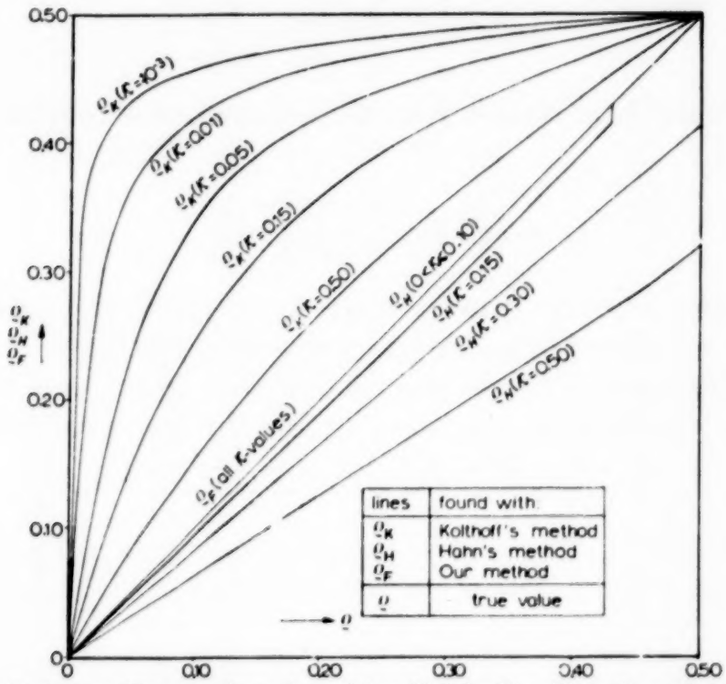

Fig. 9. Comparison between the ϱ-values found by Kolthoff's, Hahn's and our method and the true ϱ-values (effect of dilution neglected). ϱ_K, lines found by Kolthoff's method; ϱ_H, lines found by Hahn's method; ϱ_F, lines found by our method; ϱ, true value.

The dots on each curve correspond to equidistant volumes and to the four potentials — two before and two after the equivalence point — needed for determining the end-point and the ionization constant by our method.

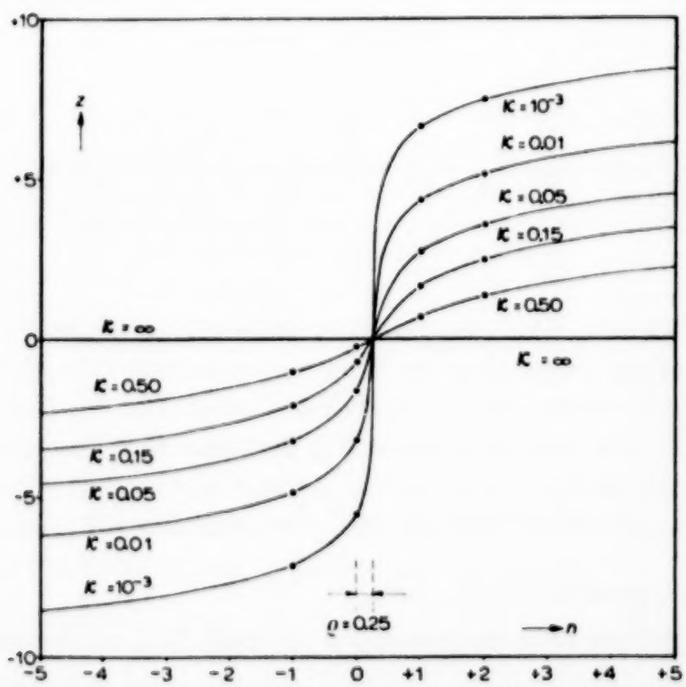

Fig. 10. Symmetric titration curve with different $\varkappa$-values (effect of dilution neglected). The lines refer to data found with eqn. (35).

Table I shows the ϱ-values found by application of the three methods to the data corresponding to the dots in Fig. 10. These data, which can also be read from Fig. 9, confirm the conclusions of the foregoing section.

TABLE I

$\varkappa$	*True value* ϱ	*Found* ϱ_K	ϱ_n	ϱ_r
10^{-3}	0.25	0.48	0.25	0.25
0.01	0.25	0.47	0.25	0.25
0.05	0.25	0.44	0.25	0.25
0.15	0.25	0.39	0.24	0.25
0.50	0.25	0.31	0.16	0.25

TABLE II TITRATION OF 45 ml KIO_3 (0.1 N HNO_3) WITH 0.100 N $AgNO_3$

Found		*Calculated*			
v *ml*	E *mV*	Δ *mV*		v_0 *ml*	K *mequiv.²/ml²*
3.80	292	} 16		$R_1 = 0.615$	$n = 0.100$
4.30	308	} 24	Δ_1	$R_2 = 0.875$	$\Delta v = 0.50$
4.80	332	} 39	Δ_0	$\varrho = 0.42$	$V = 45$
5.30	371	} 21	Δ_2	$v_e = 4.80$	$\varphi = 1.00 \cdot 10^{-2}$
5.80	392	} 12		$v_0 = 5.01$	$\varkappa = 0.28$
6.30	404				$K = 8 \cdot 10^{-8}$

Conclusion

If in a symmetric potentiometric titration the reagent is added in equal volumes Δv, the end-point lies between the volumes corresponding to the boundaries of the maximum potential step. Consequently, if Δv is very small in proportion to the total amount of reagent added at the end-point, the equivalence point can be accurately fixed without any interpolation being required. We can then agree with KOLTHOFF's statement[3], concerning the method of HAHN *et al.*[13]: "their methods do not give more information than we obtain from much simpler procedures".

If, however, an interpolation is required, we must agree with HAHN's view[8] that KOLTHOFF's method leads to inaccurate results*.

TABLE III TITRATION OF 50 ml NaCl WITH 0.100 N $AgNO_3$

Found		*Calculated*			
v *ml*	E *a.u.**	Δ *a.u.*		v_0 *ml*	K *mequiv.²/ml²*
1.50	7.59	} 22		$R_1 = 0.179$	$n = 0.100$
2.00	7.37	} 41	Δ_2	$R_2 = 0.732$	$\Delta v = 0.50$
2.50	6.96	} 312	Δ_0	$\varrho = 0.38$	$V = 50$
3.00	3.84	} 56	Δ_1	$v_e = 3.00$	$\varphi = 0.94 \cdot 10^{-2}$
3.50	3.28	} 21		$v_0 = 2.81$	$\varkappa = 0.012$
4.00	3.07				$K = 1.3 \cdot 10^{-10}$

* a.u. = arbitrary units (proportional to the potential in mV)

* The author hopes that his paper may contribute towards making peace in "the thirty years' war" about this subject between F. L. HAHN and I. M. KOLTHOFF.

EXPERIMENTAL

In order to check our method we have performed a number of potentiometric titrations. About 50 ml of each solution were carefully titrated by addition of constant increments Δv of 0.1 N reagent from a piston burette at 25° with constant stirring. The experimental data and the values derived by our method are represented in Tables II–VII.

TABLE IV TITRATION OF 50 ml KCNS WITH 0.100 N $AgNO_3$

Found		*Calculated*			
v ml	*E a.u.*	*Δ a.u.*		*v_0 ml*	*K mequiv.²/ml²*
1.50	7.38	} 7		$R_1 = 0.107$	$n = 0.100$
2.00	7.31	} 15	Δ_2	$R_2 = 0.94$	$\Delta v = 0.50$
2.50	7.16	}150	Δ_0	$\varrho = 0.48$	$V = 50$
3.00	5.66	} 16	Δ_1	$v_e = 3.00$	$\varphi = 0.94 \cdot 10^{-2}$
3.50	5.50	} 6		$v_0 = 2.76$	$\varkappa = 2 \cdot 10^{-3}$
4.00	5.44				$K = 3.5 \cdot 10^{-12}$

TABLE V TITRATION OF 50 ml HCl (IN 0.1 N NaCl) WITH 0.1000 N NaOH

Found		*Calculated*			
v ml	*pH*	*Δ a.u.*		*v_0 ml*	*K mequiv.²/ml²*
(a)					
1.50	3.12	} 17		$R_1 = 0.174$	$n = 0.100$
2.00	3.29	} 32	Δ_2	$R_2 = 0.294$	$\Delta v = 0.50$
2.50	3.61	}628	Δ_0	$\varrho = 0.09$	$V = 50$
3.00	9.89	}109	Δ_1	$v_e = 3.00$	$\varphi = 0.94 \cdot 10^{-2}$
3.50	10.98	} 22		$v_0 = 2.96$	$\varkappa = 2 \cdot 10^{-4}$
4.00	11.20				$K = 3.5 \cdot 10^{-14}$
(b)					
1.50	3.16	} 17		$R_1 = 0.157$	$n = 0.1000$
2.00	3.33	} 29	Δ_2	$R_2 = 0.290$	$\Delta v = 0.50$
2.50	3.62	}638	Δ_0	$\varrho = 0.08$	$V = 50$
3.00	10.00	}100	Δ_1	$v_e = 3.00$	$\varphi = 0.94 \cdot 10^{-2}$
3.50	11.00	} 25		$v_0 = 2.96$	$\varkappa = 1.0 \cdot 10^{-4}$
4.00	11.25				$K = 0.9 \cdot 10^{-14}$

TABLE VI TITRATION OF 50 ml NaI WITH 0.100 N $AgNO_3$

Found		*Calculated*			
v ml	*E a.u.*	*Δ a.u.*		*v_0 ml*	*K mequiv.²/ml²*
(a)					
1.50	7.78	} 9		$R_1 = 0.227$	$n = 0.100$
2.00	7.69	} 59	Δ_1	$R_2 = 0.153$	$\Delta v = 0.50$
2.50	7.10	}260	Δ_0	$\varrho = 0.01$	$V = 50$
3.00	4.50	} 9	Δ_2	$v_e = 2.50$	$\varphi = 0.95 \cdot 10^{-2}$
3.50	4.41	} 5		$v_0 = 2.50$	$\varkappa = 5 \cdot 10^{-6}$
4.00	4.36				$K = 0.23 \cdot 10^{-16}$
(b)					
1.50	7.78	} 10		$R_1 = 0.336$	$n = 0.100$
2.00	7.68	} 80	Δ_1	$R_2 = 0.113$	$\Delta v = 0.50$
2.50	6.88	}238	Δ_0	$\varrho = 0.002$	$V = 50$
3.00	4.50	} 9	Δ_2	$v_e = 2.50$	$\varphi = 0.95 \cdot 10^{-2}$
3.50	4.41	} 5		$v_0 = 2.50$	$\varkappa = 7 \cdot 10^{-6}$
4.00	4.36				$K = 0.44 \cdot 10^{-16}$

TABLE VII IONIZATION CONSTANTS AT 25°C

Substance	See Table	K value		pK value	
		Calculated	Literature[a]	Calculated	Literature
$AgIO_3$	II	$8 \cdot 10^{-8}$	$3 \cdot 10^{-8}$	7.1	7.5
AgCl	III	$1.3 \cdot 10^{-10}$	$1.7 \cdot 10^{-10}$	9.9	9.8
AgCNS	IV	$3.5 \cdot 10^{-12}$	$1.0 \cdot 10^{-12}$	11.5	12.0
H_2O	V(a)	$3.5 \cdot 10^{-14}$	$1.0 \cdot 10^{-14}$	13.5	14.0
	V(b)	$0.9 \cdot 10^{-14}$	$1.0 \cdot 10^{-14}$	14.0	14.0
AgI	VI(a)	$0.23 \cdot 10^{-16}$	$0.85 \cdot 10^{-16}$	16.6	16.1
	VI(b)	$0.44 \cdot 10^{-16}$	$0.85 \cdot 10^{-16}$	16.4	16.1

From the experimental data (Tables II–VII) we may conclude that our method is simple, requires no graphical representation of the measurements and leads to approximate values of the ionization constants.

ACKNOWLEDGEMENT

I wish to thank Mr. J. L. H. SOONS, of the Analytical Department of our Laboratory, who calculated the numerical values plotted in the figures.

SUMMARY

A method is developed for calculating the end-point and the ionization constant in a potentiometric titration. The influence of dilution is studied. The method is compared with the procedure of KOLTHOFF and that of HAHN.

RÉSUMÉ

Une méthode a été mise au point pour le calcul du point final et de la constante d'ionisation lors d'un titrage potentiométrique. On étudie l'influence de la dilution. On compare la méthode aux procédés recommandés par KOLTHOFF et par HAHN.

ZUSAMMENFASSUNG

Es wurde eine Methode zur Berechnung des Endpunktes und der Ionisationskonstante bei einer potentiometrischen Titration entwickelt. Ferner wurde der Einfluss der Verdünnung untersucht. Die Methode wurde sowohl mit dem von KOLTHOFF wie vom HAHN empfohlenen Verfahren verglichen.

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POLAROGRAPHIC ANALYSIS USING POTASSIUM IODIDE AS A SUPPORTING ELECTROLYTE*

III. THE POLAROGRAPHIC BEHAVIOR OF TRIVALENT ARSENIC

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INTRODUCTION

Polarographic studies on trivalent arsenic in 1 *M* hydrochloric acid have been reported by several authors[1-5]. KACIRKOVA[1] reported that the reduction wave of arsenious acid in this medium consisted of two steps at approximately —0.3 V and —0.6 V *vs.* SCE. The first wave which resulted from the reduction of arsenious acid to metallic arsenic was not used for quantitative analysis, but the height of the second wave was proportional to the concentration of arsenic acid.

On the other hand, LINGANE[2] found two steps with starting potentials of —0.4 V and —0.9 V *vs.* SCE in 1 *M* hydrochloric acid; the first wave height was proportional to the concentration of arsenious acid in solutions containing 0.01% gelatine as a maximum suppressor and the diffusion current constant was 8.6 at 25°. He suggested that this wave was due to the reduction of arsenic(III) to the elementary state rather than to arsine.

After that, MEITES[3] reported the polarographic characteristics of arsenious acid in the same medium without a maximum suppressor. The half-wave potential of the first step was —0.428 V *vs.* SCE and the diffusion current constant was 6.04, which is smaller than the value reported by LINGANE. The wave height of the first step was proportional to the concentration of arsenic in the range between 0.018 and 0.9 m*M*; the wave height became constant at concentrations higher than 0.9 m*M* and was independent of changes in temperature, concentration of hydrochloric acid or arsenic.

Since we have studied the polarographic behavior of several metal ions in solutions of potassium iodide as a supporting electrolyte[6-7], the usefulness of the method has been recognized for polarographic analysis, particularly as a well-separated reduction wave was given for a sample containing indium and cadmium[6].

In this paper, the polarographic behavior of trivalent arsenic is described in solutions of 0.1 to 1.0 *M* potassium iodide containing 0 to 0.0015% of dodecyl trimethyl ammonium chloride as a maximum suppressor.

EXPERIMENTAL

All polarograms were recorded by the Yanagimoto pen-recording polarograph, Model

* Parts I and II in this series were presented in the *Repts. Govt. Ind. Research Inst., Nagoya*, 8 (1959) 638; 9 (1960) 28.

PB-4. The flow rate of mercury, m, and the drop-time were respectively 1.41 mg/sec and 3.41 sec/drop at the applied potential of —0.80 V *vs.* SCE; the height of mercury column was $h = 68.5$ cm Hg. A saturated calomel electrode was used as a reference electrode and was connected to the solution through an agar bridge.

All experiments were carried out in a thermostat maintained at 25 ± 0.1°. The pH value of the solution was measured with a Horiba glass electrode pH-meter, Model M-3.

The 0.02 *M* arsenic stock solution was prepared by dissolving reagent-grade arsenic oxide in a minimal volume of 2 *N* potassium hydroxide followed by acidification with hydrochloric acid and dilution to a known volume with distilled water. A 2 *M* potassium iodide solution was used as supporting electrolyte and was prepared from analytical grade reagent. Solutions of DTAC and other surface active substances used as maximum suppressors were 0.01%.

The electrolytic sample solutions were prepared by the following procedure. To a certain volume of the stock solution of arsenic, sufficient supporting electrolyte and maximum suppressor were added to reach the final concentrations: 0.1 *M* to 1.0 *M* and 0.0005% to 0.0015%, respectively. The pH value of the sample solution was then adjusted by adding a little dilute hydrochloric acid or potassium hydroxide.

Dissolved oxygen was removed by bubbling pure nitrogen gas through the sample solution for about 15 min. Then the polarograms were recorded.

RESULTS AND DISCUSSION

The reduction waves of trivalent arsenic in 0.1 *M* potassium iodide containing DTAC as the maximum suppressor are shown in Fig. 1. The first step was a well-defined wave

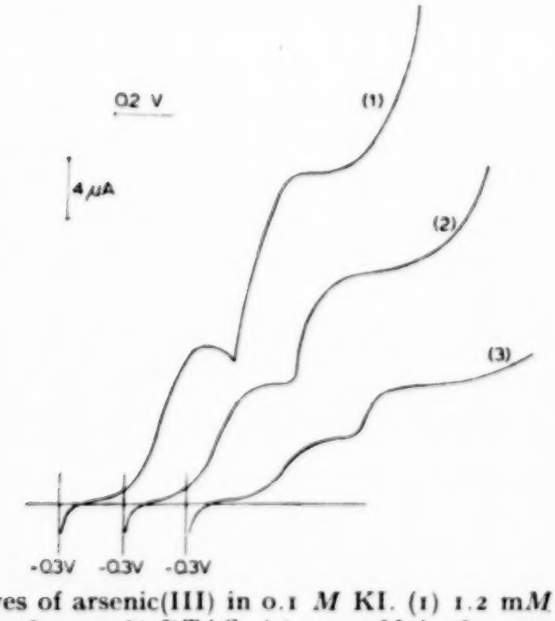

Fig. 1. The reduction waves of arsenic(III) in 0.1 *M* KI. (1) 1.2 m*M* As^{+3}, 0.001% DTAC; (2) 0.8 m*M* As^{+3}, 0.001% DTAC; (3) 0.4 m*M* As^{+3}, 0.001% DTAC.

at concentrations of arsenic less than 0.8 m*M* (Curves 2 and 3), but the wave did not show a plateau pattern at concentrations of trivalent arsenic higher than 1.0 m*M*. The reduction current rose slowly and fell with increasing applied potential, *i.e.* the wave developed a roundish pattern (Curve 1).

The second wave, in the absence of a maximum suppressor, had a curious double maximum wave which could not be suppressed by gelatine (Fig. 2, Curve 1); several surface-active substances were tested as maximum suppressors and DTAC was found to be the most useful. The effects of DTAC on the reduction wave of trivalent arsenic in 0.1 *M* potassium iodide are shown in Fig. 2. The same characteristics as in the first wave are indicated.

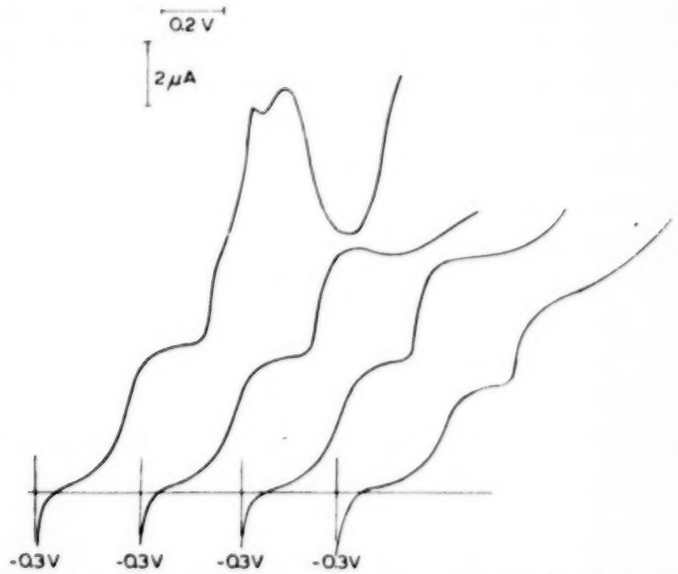

Fig. 2. The effect of DTAC on the reduction waves: As^{+3}, 0.4 m*M*; KI, 0.1 *M*; pH = 2.1 to 2.3. (1) DTAC 0; (2) DTAC 0.0005%; (3) DTAC 0.0010%; (4) DTAC 0.0015%.

Influence of the effective pressure on the dropping mercury electrode and of temperature on the limiting current

When the heights of mercury column were altered, the limiting current of the first wave or the total wave was recorded both in the absence and presence of DTAC. Tables I, II and III show the results. The limiting currents of the first wave in the absence of DTAC and those of the first wave or total wave in the presence of DTAC were proportional to the square root of the effective height on the mercury column (corrected for the back pressure).

The temperature coefficients of the limiting current in the presence and absence of DTAC were found to be 1.4% and 1.7% per 1°C, respectively.

From these results, it is considered that the limiting currents in the case described are diffusion-controlled.

TABLE I

RELATION BETWEEN LIMITING CURRENT AND MERCURY PRESSURE ON THE FIRST WAVE

h(cm)	h_{corr}	i_l (μA)	i_l/h_{corr}
53.5	7.20	3.02	0.420
57.5	7.47	3.08	0.416
61.5	7.79	3.16	0.409
65.5	7.99	3.25	0.409

KI, 0.1 *M*; As^{+3}, 0.4 m*M*; pH, 2.45.

TABLE II

RELATION BETWEEN LIMITING CURRENT AND MERCURY PRESSURE ON THE FIRST WAVE

h(cm)	h_{corr}	As^{+3} (mM)	i_l	i_l/h_{corr}
63	7.810	0.8	5.97	0.764
67	8.062	0.8	6.45	0.800
71	8.426	0.8	6.43	0.763
75	8.544	0.8	6.79	0.795
KI, 0.1 M; DTAC, 0.001%; pH, 2.48.				
63	7.810	0.4	2.75	0.353
67	8.062	0.4	2.87	0.356
71	8.426	0.4	3.03	0.359
75	8.544	0.4	3.08	0.360
KI, 0.1 M; DTAC, 0.001%; pH, 2.38.				

TABLE III

RELATION BETWEEN LIMITING CURRENT AND MERCURY PRESSURE ON THE TOTAL WAVE

h(cm)	h_{corr}	As^{+3} (mM)	i_l (μA)	i_l/h_{corr}
63	7.810	0.8	12.77	1.64
67	8.062	0.8	13.17	1.63
71	8.426	0.8	13.53	1.61
75	8.544	0.8	13.95	1.63
KI, 0.1 M; DTAC, 0.001%; pH, 2.48.				
63	7.810	0.4	6.121	0.784
67	8.062	0.4	6.362	0.789
71	8.426	0.4	6.573	0.780
75	8.544	0.4	6.704	0.785
KI, 0.1 M; DTAC, 0.001% pH, 2.48.				

The effects of pH on the reduction wave

The effects of pH on the half-wave potential and the diffusion currents were studied; the characters of the arsenic(III) reduction wave in the pH range 1.90 to 2.76 are shown in Figs. 3 and 4. Below pH 1.9, the starting point of the first wave was so close to the anodic wave of dissolution of mercury that measurements of the wave height were very difficult. The height of the first wave decreased with increasing pH in the range 1.90 to 2.50, but the total wave height showed a constant value (Fig. 3). Above pH 3.00, the wave height apparently decreased with increasing pH. The results indicate that the reduction of trivalent arsenic decreases with a decrease in the concentration of hydrogen ions.

The half-wave potentials of both the first and second waves shifted to more negative values with increasing pH; the second wave shifted farther than the first (Fig. 4). The relationship between the half-wave potential of the first wave and the pH was linear, with the gradient about 115 mV per pH unit. The reduction of arsenious acid at the dropping mercury electrode is considered to proceed as follows:

$$AsO_2^- + 4\,H^+ + 3\,e \rightarrow As^0 + 2\,H_2O \qquad (1)$$

Therefore, the relationship between the half-wave potential and pH can be written

$$E_{1/2} = E_0 - \frac{0.059}{n} m \text{ pH} + \frac{0.059}{n} \ln \frac{f_R\sqrt{D_O}}{f_O\sqrt{D_R}} \quad (2)$$

where f_R and f_O are the activities of the reductant and oxidant respectively, and D_R and D_O are the corresponding diffusion coefficients. If the reaction proceeds reversibly, $n = 3$ and $m = 4$, and the value of $\Delta E_{1/2}$ per pH unit should be 80 mV from eqn. (2). But the value found showed greater shifts than would be expected if the reaction proceeded reversibly.

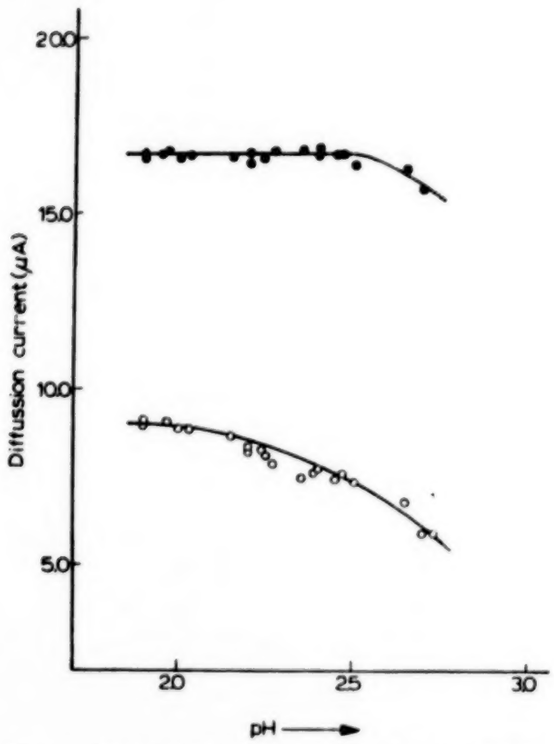

Fig. 3. The effect of pH on the wave height: As^{+3}, 1.0 mM; KI, 0.1 M; pH = 1.9 to 3.5. —●—●— total wave; —o—o— first wave.

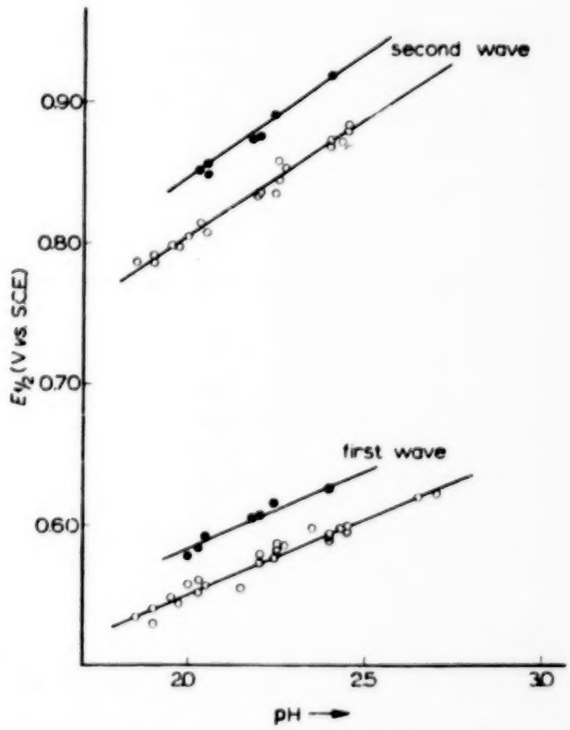

Fig. 4. The effect of pH on the half wave potential: As^{+3}, 1.0 mM; KI, 0.1 M (—●—●—) and 1.0 M (—o—o—); pH = 1.9 to 3.5.

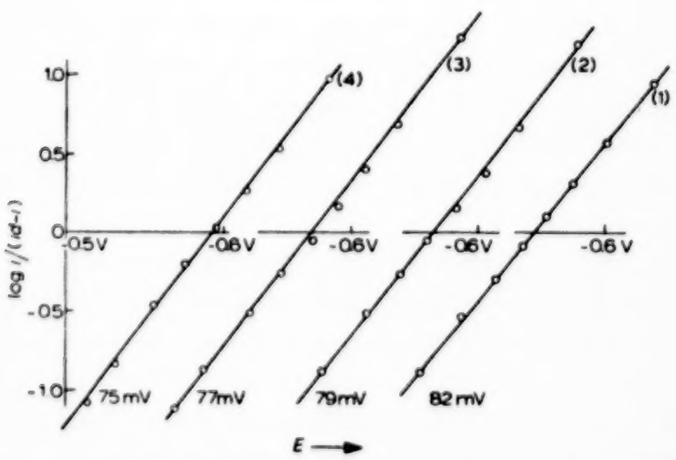

Fig. 5. The plots of $E - \log[i/(i_d - i)]$ of the first wave at several pH values: (1) pH = 2.00, (2) pH = 2.20, (3) pH = 2.25, (4) pH = 2.45. The values shown at the foot of each curve are the reciprocal slopes.

In order to learn more about the nature of the irreversible reduction of trivalent arsenic in potassium iodide solution, the reduction wave was analysed by a logarithmic plot. As shown in Fig. 5, the plots of $E - \log i/(i_d - i)$ of the first wave showed a linear dependence at pH values of 2.00, 2.20, 2.25 and 2.45; the gradients are indicated in Fig. 5. Therefore, one can conclude that the reaction $As^{+3} \rightarrow As^0$ is irreversible, because the reciprocal slope of the first wave showed a value greater than the theoretical (three electrons). The reciprocal slope of the first wave at a certain pH is not a constant, the value decreasing with increasing pH. It is evident that the irreversible reaction of trivalent arsenic is dependent on the pH of the solution.

Relation between the reduction current and trivalent arsenic concentration

When concentrations varying from 0.06 m*M* to 4.00 m*M* of arsenious acid were adjusted to pH 2.0 to 2.4, and the reduction waves were recorded, the height of the first reduction wave increased proportionally to the concentration of arsenic only in the range from 0.06 m*M* to 0.8 m*M* (Fig. 6, A and B); however, above 1.0 m*M* of

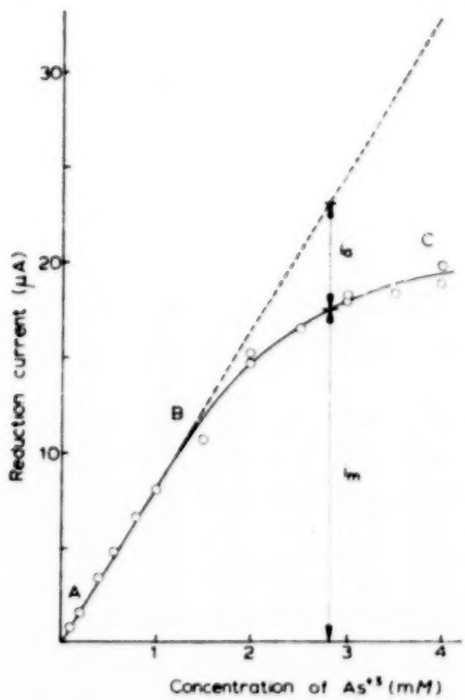

Fig. 6. Relation between the reduction current and the concentration of As^{+3} in 0.1 *M* KI. The broken line shows the value extrapolated from the linear at low concentrations.

arsenic the relation between the reduction wave height and the concentration was not linear (Fig. 6, B and C), and the diffusion current constant decreased with increasing concentrations of arsenious acid. The reproducibilities of the reduction current were not good in the range 1.0 m*M* to 2.5 m*M* of arsenious acid, but were better at higher concentrations.

It is interesting that the point B at which the concentration began to show non-linearity (in Fig. 6) agreed with the point at which the plateau of the first wave changed to a roundish curve (Fig. 1, Curve 1). In an explanation suggested by MEITES[3],

it is considered that a film of elemental arsenic adsorbed on the surface of the mercury drop limits the regular diffusion of trivalent arsenic. This adsorption phenomenon was confirmed from the relationship of the concentration and wave height. The difference between the observed current at non-linear relationships and the current extrapolated to a linear relationship between wave height and concentration of arsenic is considered as an adsorption phenomenon. From a general equation of isothermal adsorption, the following equation can be written

$$i_c - i_m = i_a = aC^{1/n}$$

Therefore,

$$\log i_a = \log a + \frac{1}{n} \log C$$

where i_c is the current extrapolated to a linear relation, i_m is the observed current height at non-linear relation, i_a is the difference of these two currents (in Fig. 6), and C is the concentration of arsenic. The plots of log i_a against log C show a linear relationship (Fig. 7), consequently a non-linear relationship between the reduction wave

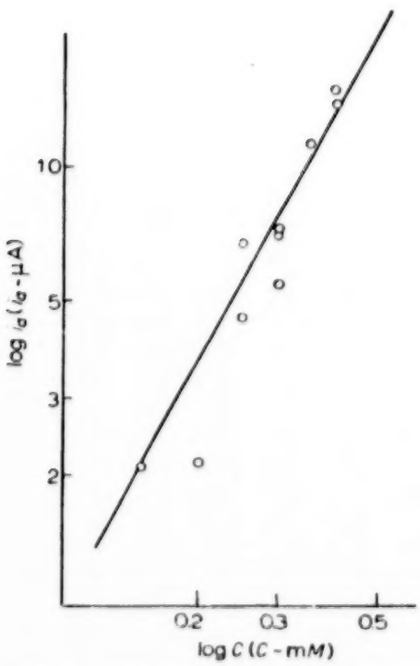

Fig. 7. The adsorption effect of the arsenic concentration on the reduction current.

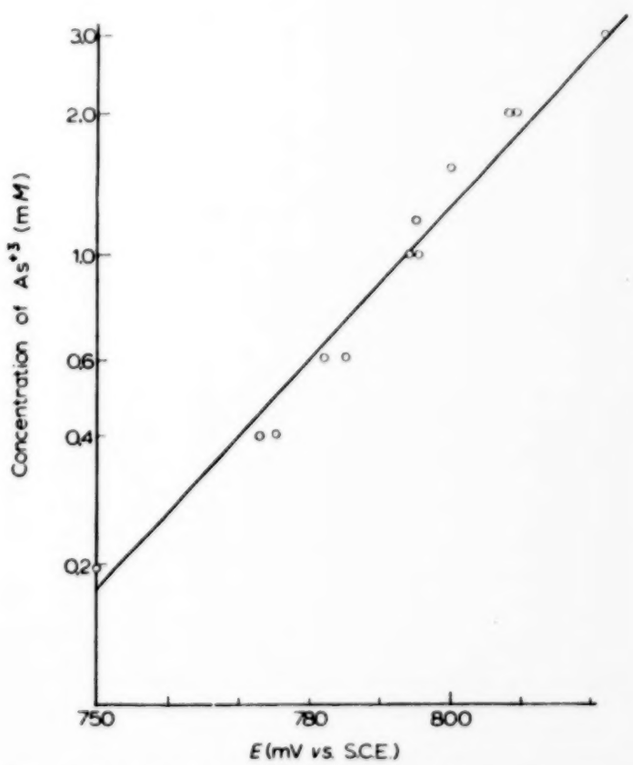

Fig. 8. The effect of the arsenic concentration on the starting potential of the second reduction wave.

height and the concentration can be considered as some effect of an adsorption phenomenon upon the reduction process of arsenic at the surface of the mercury drop.

The reduction current under the conditions of the adsorption phenomenon formed a round pattern with increasing negative potential; the second reduction current appeared suddenly at the end of the drop in the roundish pattern. The curvature of the rounded wave increased with increasing concentrations of arsenious acid, and

the starting potential of the second reduction wave also shifted to negative potentials with increasing concentrations of arsenious acid. The results are given in Fig. 8.

The phenomenon is considered as follows. The amount of arsenic adsorbed on the surface of mercury drop increases with shifting negative potentials and the reduction current decreases. At the potential corresponding to the active energy for reduction of the second wave, a sharp reduction current appears. The phenomenon is found notably with increasing concentrations of arsenic; it is considered that the starting potentials of the second wave become more negative, increasing active energy being necessary for reduction of the second wave.

The relationship between the total wave height (the first and second wave heights) and the concentration of arsenious acid is shown in Table IV; the relationship below

TABLE IV

RELATION BETWEEN THE TOTAL WAVE HEIGHT AND THE CONCENTRATION OF ARSENIC

	As^{+3} (mM)	i_d (μA)	$i_d C$	I
	0.06	0.957	15.95	10.33
	0.10	1.601	16.01	10.33
	0.20	3.271	16.35	10.59
	0.40	6.593	16.48	10.68
	0.60	9.735	16.23	10.51
	0.80	12.98	16.23	10.51
	1.00	16.63	16.63	10.77
	2.00	33.58	16.78	10.87
	3.00	51.11	17.03	11.03
	4.00	67.04	16.79	10.86
Mean			16.45 ± 0.36	10.65 ± 0.23

KI, 0.1 M; DTAC, 0.001%; pH, 2.1 to 2.3; $m^{2/3} t^{1/6}$, 1.543.

the concentration 4.0 mM is linear and the total wave height at constant concentration is a constant value over the pH range 1.9 to 2.5. Therefore, the polarographic determination of micro amounts of arsenic in potassium iodide solution seems to be possible.

SUMMARY

The polarography of arsenic(III) in 0.1 or 1.0 M potassium iodide solutions has been studied.

RÉSUMÉ

Les auteurs ont effectué une étude du comportement polarographique de l'arsenic(III), en utilisant l'iodure de potassium comme électrolyte de base.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das polarographische Verhalten von Arsen(III) bei Verwendung von Kaliumjodid als Grundelektrolyt.

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CONTRIBUTIONS TO THE COMPLEXOMETRIC DETERMINATION OF CATION MIXTURES

III. SIMULTANEOUS TITRATION OF IRON(III) AND ALUMINIUM IN THE PRESENCE OF AMMONIUM THIOCYANATE AS INDICATOR*

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The possibility of determining metals by titration of the excess of EDTA with a cobalt solution in the presence of thiocyanate indicator was described by TAKAMOTO[2]; SEN[3] has indicated that it is necessary for log K_{MY} to be greater than or equal to 15.

Owing to the fact[4] that log $K_{CoY} = 16.31$ and log $K_{AlY} = 16.13$, the reaction

$$AlY^{-} + Co^{+2} \rightarrow CoY^{-2} + Al^{+3}$$

may be possible; hence the end-point may not be stable. But in this titration, as well as when the excess of EDTA is back-titrated with iron(III) solution in presence of salicylic acid or sulfosalicyclic acid where $K_{FeY} \gg K_{AlY}$, the end-point is sufficiently stable to be observed, because the decomposition as well as the formation of the aluminium–EDTA complex takes place at a reduced rate.

In the present work a method for the determination of aluminium(III) is described in which excess of EDTA is back-titrated with cobalt nitrate solution in acetone–water medium containing thiocyanate as indicator; the simultaneous determination (in the same solution) of aluminium(III) and iron(III) is also described.

EXPERIMENTAL

The aluminium solution (0.05 *M*) was prepared from $AlCl_3 \cdot 6H_2O$ and standardized by precipitation of the aluminium as hydroxide and calcination to Al_2O_3; the iron solution (0.05 *M*) was prepared from $FeCl_3 \cdot 6\ H_2O$ and standardized by precipitation of the iron as hydroxide and calcination to Fe_2O_3 and the EDTA solution (0.05 *M*) was prepared from disodium ethylenediaminetetraacetate.

PROCEDURE

To 10 ml of solution containing 1–30 mg of aluminium(III) and 0.5–6 mg of iron(III) at pH *ca.* 2, were added 5 drops of ammonium thiocyanate solution (1%) and the mixture was titrated with 0.05 *M* EDTA solution until the red color of the solution

* Part II: See ref.[1].

changed to yellow. Iron(III) was thus determined. For the determination of the aluminium a measured excess of 0.05 *M* EDTA solution was then added to the solution. The pH was adjusted to 5–7 with a few drops of a concentrated sodium hydroxide solution and ammonium acetate (1 g) and then a saturated solution of ammonium thiocyanate (1 ml) and acetone were added to the solution. The volume of the added acetone was large enough to give at the end-point of the titration a water–acetone ratio of approximately 1:1. The excess of EDTA was then titrated with 0.05 *M* cobalt nitrate solution; during the titration the yellow color of the solution changed gradually to pink-orange until at the equivalence-point it became blue-green (if the solution did not contain iron the color of the solution changed from pink to greyish-blue). The end-point was reversible. In order to obtain a sharp end-point the excess of EDTA should be sufficient to react with at least 3 ml of 0.05 *M* cobalt solution. If the ratio $[Fe^{+3}]/[Al^{+3}]$ exceeds 1/4, the end-point is not sufficiently sharp because the color changes from yellow to greenish-yellow. The results are given in Table I.

TABLE I

Aluminium taken mg	*Aluminium found (average)* mg	*Error (average)* %	*Iron(III) taken* mg	*Iron(III) found (average)* mg	*Error (average)* %
2.70	2.72	+0.74	—	—	—
6.76	6.74	−0.29	—	—	—
13.52	13.44	−0.58	—	—	—
27.04	26.86	−0.66	—	—	—
2.70	2.70	0.00	0.55	0.55	0.00
2.70	2.70	0.00	1.37	1.37	0.00
2.70	2.69	−0.36	2.74	2.74	0.00
6.76	6.78	+0.29	0.55	0.55	0.00
6.76	6.76	0.00	2.74	2.73	−0.35
6.76	6.75	−0.14	5.49	5.50	+0.18

CONCLUSIONS

The low decomposition rate of the aluminium–EDTA complex makes possible the indirect determination of aluminium(III) by back-titration of excess of EDTA with cobalt(II) solution in the presence of thiocyanate as indicator in acetonic solution.

When ammonium thiocyanate is used as indicator it is possible to titrate the iron(III) and the aluminium in the same solution if the ratio $[Fe^{+3}]/[Al^{+3}]$ is less than or equal to 1/4.

The proposed procedure is simpler than previous complexometric methods[5,6] for the simultaneous determination of iron(III) and aluminium. It has the advantages of requiring a very common indicator and of being comparatively insensitive to variations in the pH value of the solutions.

SUMMARY

With thiocyanate as indicator iron(III) and aluminium(III) can be titrated simultaneously if $[Fe^{+3}]/[Al^{+3}] \leqq 1/4$; iron(III) is titrated directly with EDTA, and aluminium(III) is determined by back-titration of the excess of EDTA with cobalt nitrate solution in an acetone–water medium.

RÉSUMÉ

En utilisant thiocyanate comme indicateur, il est possible de doser Fe^{+3} et Al^{+3} sur une même solution, si le rapport $[Fe^{+3}]/[Al^{+3}] \leqq 1/4$. Dans ce cas, on dose Fe^{+3} par titrage direct avec EDTA et Al^{+3} par titrage de l'excès de EDTA avec une solution de nitrate de cobalt en acetone–eau.

ZUSAMMENFASSUNG

Mit Thiocyanat als Indikator ist es möglich in der gleichen Lösung Fe^{+3} und Al^{+3} zu bestimmen, wenn das Verhältnis $[Fe^{+3}][Al^{+3}] \leqq 1/4$ ist. Man bestimmt das Eisen(III) direkt mit EDTA, das Aluminium indirekt durch Titration des überschüssigen EDTA mit einer $Co(NO_3)_2$ Lösung im Aceton–Wasser System.

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Short Communications

Concentrating traces of copper from 1 *M* ammonium chloride

RICHES[1] separated traces of transition metals from solutions of 0.1 *M* ammonium chloride by ion exchange. He passed 2 ml of a solution about $4 \cdot 10^{-4}$ *M* with respect to transition metal and 0.1 *M* with respect to ammonium chloride through a 1-ml bed of Amberlite IR-100, a sulfonated phenolic resin. He then removed the transition metals from the resin by washing with 1 *M* hydrochloric acid. Thus he obtained the following recoveries: 87% copper, 96% cadmium, 95% nickel, 93% zinc, and 87% manganese. This procedure was not successful when the transition metal was dissolved in 1 *M* ammonium chloride.

The abnormally great affinity of Dowex Chelating Resin A-1 toward transition metals led the authors to try a modification of RICHES' experiments with this resin. The resin has groups of $—CH_2N(CH_2COOH)_2$ attached to a matrix of crosslinked polystyrene[2]. It consisted of spherical particles, mostly in the range of 40–50 mesh.

A solution was prepared to be $1.58 \cdot 10^{-4}$ *M* with respect to cupric chloride and 1 *M* with respect to ammonium chloride. After standardization, this was diluted 1:10 with 1 *M* ammonium chloride to give a solution 1 *M* in ammonium chloride and $1.58 \cdot 10^{-5}$ *M* in copper, or containing 1.00 p.p.m. of copper.

1-l portions of this solution were passed through columns of the ammonium form of Dowex A-1. The copper was then removed from the columns with 10 ml of 1 *M* hydrochloric acid and determined by titration with 0.01 *M* ethylenediaminetetraacetate[3].

The results are summarized in Table I. Recoveries of 99% or better were obtained in all experiments except those with bed volumes less than 1.0 ml (numbers 1, 5 and 9) or with flow rates greater than 3.8 cm/min (numbers 7, 8 and 9). It is obvious that

the chelating resin is much more effective than ordinary cation-exchange resins in the recovery of traces of copper from fairly concentrated solutions of ammonium chloride. The chelating resin will probably serve equally well in concentrating traces of other transition metals from solutions of alkali metals and possibly also from the alkaline-earth metals.

TABLE I

RECOVERY OF $1.58 \cdot 10^{-5}$ *M* COPPER FROM 1 *M* AMMONIUM CHLORIDE

No.	*Column dimensions* *cm*	*cm²*	*Flow rate* *cm/min*	*Recovery* *%*
1	1.0	0.94	0.80	96.7
2	1.7	0.94	1.52	99.6
3	1.4	0.94	2.24	99.0
4	1.1	0.94	3.01	99.2
5	1.0	0.94	3.28	98.9
6	1.2	0.94	3.75	99.1
7	1.3	0.94	4.00	93.5
8	1.1	0.94	5.52	93.0
9	1.0	0.94	6.00	88.5

The authors express their gratitude to The Dow Chemical Company, Midland, Michigan, for financial support of this investigation.

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Anal. Chim. Acta, 24 (1961) 202–203

A rapid and sensitive sub-micro phosphorus determination

A method for increasing the sensitivity of the phosphorus determination proposed by FISKE AND SUBBAROW[1] has recently been introduced by BARTLETT[2]. Such increased sensitivity is necessary for the examination of small phospholipid fractions from chromatographic columns, and samples of 50 to 150 μg organic material can be successfully analysed by this technique. The modification lies[2] in carrying out the reduction of phosphomolybdate with 1-amino-2-naphthol-4-sulphonic acid (ANSA) at 100° instead of at room temperature and in measuring the absorption at 830 mμ instead of at 660 mμ.

In our experience the method gives good results: the reproducibility is excellent

and the colour is stable for at least 24 h. A further advantage is that the coloured solution can be diluted with distilled water for measurement in the most sensitive range of the spectrophotometer without loss of proportionality. The sensitivity is 0.1 μg of P (extinction of 0.051 with a 3-cm cuvette). A grave disadvantage of the procedure is, however, that the initial digestion of the sample to give phosphate ion (heating with sulphuric acid at 160–180°) requires 4½ h for completion. Increasing the temperature of the digestion mixture is not favourable because of the risk of loss of phosphoric acid (b.p. 213°). Perhydrol added to decrease the reaction time is difficult to remove completely.

We have found that perchloric acid, as used by ALLEN[3] in his method employing amidol as reducing agent, is a better agent for the first step, in that the time necessary for complete digestion can then be reduced to 40 min. (We have established, incidentally, that amidol is not a suitable reducing agent for the development of the colour at 100°, since it gives irreproducible results at this temperature.)

Samples were heated, after the removal of organic solvents, with 0.2 ml of 70% perchloric acid in tubes (125 × 15 mm) standing to a depth of 30 mm in a thermostatically controlled heating block maintained at 180°. The boiling mixture generally cleared after 12 to 18 min heating, and the reaction was completed by heating for a further 20 min. That the reaction was not complete when the mixture first cleared was established by stopping the reaction at this point by rapid cooling; recoveries of only 94–97% were obtained.

Using the described 40-min digestion procedure, and the method of colour development as recommended by BARTLETT, we obtained the following results for a solution of tritotyl-phosphate of high purity (May and Baker Ltd.) in methanol (see Table I).

TABLE I

P added (µg)	*P found (µg)*	*Recovery (%)*
1.09	1.11	101.8
1.81	1.81	100.0
2.54	2.51	98.8
3.63	3.64	100.3

It is suggested that the modification of the digestion procedure described should enhance considerably the usefulness of the sensitive BARTLETT determination.

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THE VOLUMETRIC ANALYSIS OF PHOSPHATES

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The determination of total P_2O_5 and of borate are important features of the analysis of detergent powders. Until recently we had always done the former by the standard magnesium pyrophosphate method. This method is tedious, and although it has the advantage of removing the phosphate from solution it does not render the borate readily accessible. We decided to try to develop an alternative method for the phosphate, which must be rapid, simple in operation, reliable and accurate, bring about removal of the phosphate and facilitate the subsequent determination of borate on the same solution. The requirement that the method should be rapid meant that it would have to be either colorimetric or volumetric. There are many colorimetric methods, most of which are variants of either DENIGÈS' method[1] in which phosphomolybdic acid is reduced to molybdenum blue, or of the phosphovanadomolybdate method first described by MISSON[2]. These are rapid and accurate, but do nothing towards making the borate more accessible. There are at least two volumetric methods[3,4] based on the precipitation of phosphomolybdate but in both cases the excess reagents would increase the difficulty in the determination of borate. Other volumetric methods include those by THISTLETHWAITE[5] using bismuth, by RANCKE-MADSEN AND KJAERGARD[6] using cerium and a number of procedures all essentially the same as that described by CALAMARI AND HUBATA[7] which involves titration between two pH values. In addition many authors[8–13] have used the general principle of titrating the acid liberated when mono- or dihydrogen orthophosphates are treated with silver ion. FLATT AND BRUNISHOLZ[14] developed a potentiometric titration with silver which they described as "of limited accuracy" and an alternative method in which the phosphate was precipitated with excess silver. The precipitate was filtered off and the excess silver titrated with thiocyanate.

We attempted this last process independently and found difficulty in ensuring quantitative precipitation of the silver phosphate. Eventually we developed a method in which quantitative precipitation was achieved by titrating the liberated acid. We thus produced a technique essentially like the group of methods[8–13] already mentioned, but differing in some important details. For example, other workers had used various indicators to determine the end-point where we used a pH-meter. The latter gave greatly increased accuracy and showed that the indicators had not always been well-chosen. (We did try using methyl red and bromocresol green, but found that both were adsorbed by the precipitate). Systematic study showed that the new technique was not only rapid, simple and reliable, but also gave excellent precision and permitted the subsequent determination of borate by a sequence of operations

taking only about 15 min. We also observed that if we started with the diacid form, not only orthophosphates but also condensed phosphates would yield two equivalents of titratable hydrogen ion per molecule, and this was utilised in a new method for determining the average number of phosphorus atoms per molecule in condensed phosphates.

PRINCIPLES

For the determination of orthophosphate two reactions are of possible use:

$$Na_2HPO_4 + 3\ AgNO_3 \rightarrow Ag_3PO_4\downarrow + 2\ NaNO_3 + HNO_3$$

$$NaH_2PO_4 + 3\ AgNO_3 \rightarrow Ag_3PO_4\downarrow + NaNO_3 + 2\ HNO_3$$

The first of these was used by GERBER AND MILES for the determination of orthophosphate in condensed phosphates. The initial pH to which the solution must be adjusted before addition of the silver nitrate is 9.2 in the first case and 4.5 in the second. The end-point in the subsequent titration occurs at a pH of 4.8 in the presence of ammonium ions and at 6.0 in their absence. Interference from salts of weak acids, such as borates and silicates, would therefore be more serious if the monoacid salt were used as the starting material than if the diacid salt were used, and we accordingly chose the latter. In order to minimise such interference most of the experimental titrations were done in the presence of ammonium nitrate. This was found later to be undesirable when borate was to be determined on the same solution, and a series of experiments was performed to show that omission of the ammonium salt did not cause significant error.

It is important to keep the concentration of ammonium ion low, however, as the following experiment showed. The pH of a 5% silver nitrate solution was found to be 5.9 and that of a 20% ammonium nitrate solution 4.8. Equal volumes of the two solutions were mixed together; the pH of the mixture was 3.5. In the absence of any interaction the expected pH would be approximately 5.1. The hydrogen ions responsible for this drop in pH are presumably liberated in the formation of argentodiammine:

$$Ag^+ + 2\ NH_4^+ \rightleftharpoons Ag(NH_3)_2^+ + 2\ H^+$$

In all the titrations described in this paper the "blank" due to ammonium ions was less than 0.02 ml and was considered negligible.

PROCEDURE

Place a sample containing approximately 1 g or 0.1 g of P_2O_5, present as orthophosphate, in a 400-ml beaker. Insert pH meter electrodes and an electric stirrer. Add 100 ml of water, or more if necessary to immerse the electrodes. With the stirrer running, add 3 *N* nitric acid if necessary to bring the pH below 4.5. Adjust the pH to lie in the range 4.5 to 4.6 by addition of standard sodium hydroxide. If approximately 1 g of P_2O_5 was taken, use *N* alkali for this adjustment and the subsequent titration; for the smaller sample use 0.1 *N* alkali. Add 5 ml of 20% ammonium nitrate if *N* alkali is being used, or 1 ml if 0.1 *N* alkali is being used. Finally add the calculated amount of 10% silver nitrate (see below) and titrate with standard sodium hydroxide until the pH lies in the range 4.8 to 4.9.

1 ml *N* sodium hydroxide = 0.0355 g P_2O_5
1 ml 0.1 *N* sodium hydroxide = 0.00355 g P_2O_5

The volume of silver nitrate to be used is approximately three times the expected titration for a 1-g sample and one-tenth of this amount for a 0.1-g sample. This should be a sufficient excess, but it is advisable to add a further 5 ml at the end of the titration. More than a fractional drop in the indicated pH shows that insufficient silver nitrate was added.

RESULTS

The method was tested on 0.5 *M* and 0.05 *M* solutions of disodium hydrogen phosphate. 10-ml and 25-ml portions were analysed as described, both alone and in the presence of other salts which are commonly found in detergent powders. As a check on the completeness of precipitation the silver phosphate was filtered off, dissolved in 3 *N* nitric acid and titrated with 0.1 *N* ammonium thiocyanate using ferric alum as the indicator. In the series using 0.5 *M* phosphate the solution was diluted to 250 ml and a 25-ml aliquot used for this titration. Note that in the precipitation of one mole of silver phosphate two equivalents of hydrogen ion are liberated but three equivalents of silver ion are consumed. The thiocyanate titration should therefore be 1.5 times as great as the alkali titration.

The figures quoted in the tables of results under the heading "Theoretical titration" were determined by titration with standard acid between pH 9.15 and pH 4.55, these being the determined points of inflexion.

TABLE I

TITRATION OF 10 ml 0.5 *M* Na_2HPO_4

Foreign salt	*Amount of foreign salt*	*Theoretical titration ml N NaOH*	*Actual titration ml N NaOH*	*NH_4CNS titration ml 0.1 N*
—	—	10.01	10.01	—
—	—	10.01	10.03	14.88
—	—	10.01	10.05	14.88
—	—	10.01	10.05	14.89
—	—	10.01	10.04	14.89
$NaBO_2$	10 ml 0.1 *M*	10.01	10.02	14.93
$NaBO_2$	10 ml 0.1 *M*	10.01	10.02	14.93
$NaBO_2$	10 ml 0.1 *M*	10.01	10.04	14.90
$NaBO_2$	10 ml *M*	10.01	10.06	14.88
$NaBO_2$	10 ml *M*	10.01	10.08	14.86
$NaBO_2$	10 ml *M*	10.01	10.10	14.90
Na_2SO_4	20 g	8.87	8.86	—
Na_2SO_4	20 g	8.87	8.86	—
Na_2SO_4	20 g	8.87	8.92	—
A.A.S.[a]	2 g	8.87	8.30	unfilterable
A.A.S.[a]	2 g	8.87	8.30	unfilterable
A.A.S.[a]	2 g	8.87	8.28	unfilterable
Na_2SiO_3	1 g	8.87	8.98	—
Na_2SiO_3	1 g	8.87	8.98	—
Na_2SiO_3	1 g	8.87	8.96	—

[a] A.A.S. = sodium alkylaryl sulphonate.

TABLE II

TITRATION OF 25 ml 0.5 *M* Na_2HPO_4

Foreign salt	*Amount of foreign salt*	*Theoretical titration ml N NaOH*	*Actual titration ml N NaOH*	*NH_4CNS titration ml 0.1 N*
—	—	25.02	24.98	37.39
—	—	25.02	25.00	37.40
—	—	25.02	25.00	37.40
—	—	25.02	25.00	37.40
$NaBO_2$	25 ml 0.1 *M*	25.02	25.11	—
$NaBO_2$	25 ml 0.1 *M*	25.02	25.09	37.40
$NaBO_2$	25 ml 0.1 *M*	25.02	25.08	37.40
$NaBO_2$	25 ml 0.1 *M*	25.02	25.10	37.40
$NaBO_2$	25 ml 0.1 *M*	25.02	25.07	37.40
$NaBO_2$	25 ml *M*	22.18	22.18	33.18
$NaBO_2$	25 ml *M*	22.18	22.17	33.20
$NaBO_2$	25 ml *M*	22.18	22.18	33.20
Na_2SO_4	50 g	22.18	21.12	34.90
Na_2SO_4	50 g	22.18	20.74	—
Na_2SO_4[a]	50 g	22.18	21.70	—
Na_2SO_4[b]	50 g	22.18	21.87	34.88
Na_2SO_4[c]	50 g	22.18	22.12	34.80
Na_2SO_4[c]	50 g	22.18	22.17	34.94
Na_2SO_4[c]	50 g	22.18	22.16	35.00
Na_2SO_4[c]	50 g	22.18	22.14	35.03
Na_2SO_4	20 g	22.18	22.14	33.38
Na_2SO_4	20 g	22.18	22.12	33.35
Na_2SO_4	20 g	22.18	22.12	33.35
A.A.S.	5 g	22.18	19.86	unfilterable
A.A.S.[c]	5 g	22.18	22.90	unfilterable
A.A.S.	5 g	22.18	19.88	unfilterable
A.A.S.	1 g	22.18	20.56	unfilterable
A.A.S.	1 g	22.18	20.52	unfilterable
Na_2SiO_3	1 g	22.18	22.33	—
Na_2SiO_3	1 g	22.18	22.35	—
Na_2SiO_3	1 g	22.18	22.33	—
Na_2CO_3	1 g	22.18	22.35	—
Na_2CO_3	1 g	22.18	22.35	—

[a] 80 ml of 10% silver nitrate
[b] 90 ml of 10% silver nitrate
[c] 100 ml of 10% silver nitrate
70 ml of 10% silver nitrate was used in all those experiments not marked with superscripts.

EFFECT OF OMITTING AMMONIUM NITRATE

A further set of titrations was carried out using 0.5 *M* and 0.05 *M* phosphate, to see whether the omission of ammonium nitrate would have an adverse effect. 10-, 25- and 50-ml portions of each solution were analysed by the method described, using 10 ml of 20% ammonium nitrate in each of the experiments with 0.5 *M* phosphate and 1 ml in each of those with 0.05 *M* phosphate. These two series were then repeated with the omission of the ammonium nitrate, the final titration now being taken to a pH of 6.0. In the series with 0.5 *M* phosphate there was no significant difference between the experiments with and without ammonium nitrate, but in the series with 0.05 *M*

TABLE III

TITRATION OF 10 ml 0.05 *M* Na_2HPO_4

Foreign salt	*Amount of foreign salt*	*Theoretical titration ml 0.1 N NaOH*	*Actual titration ml 0.1 N NaOH*	*NH_4CNS titration ml 0.1 N*
—	—	10.00	9.67	14.42
—	—	10.00	9.63	14.42
—	—	10.00	9.63	14.45
$NaBO_2$	10 ml 0.1 *M*	10.00	9.96	14.98
$NaBO_2$	10 ml 0.1 *M*	10.00	9.98	14.98
$NaBO_2$	10 ml 0.1 *M*	10.00	9.96	15.00
Na_2SO_4	5 g	10.00	9.95	—
Na_2SO_4	5 g	10.00	9.98	—
Na_2SO_4	5 g	10.00	9.95	—
Na_2SiO_3	0.2 g	10.00	9.98	—
Na_2SiO_3	0.2 g	10.00	10.00	—
Na_2SiO_3	0.2 g	10.00	9.98	—
Na_2CO_3	0.1 g	10.00	10.00	—
Na_2CO_3	0.1 g	10.00	9.97	—

TABLE IV

TITRATION OF 25 ml 0.05 *M* Na_2HPO_4

Foreign salt	*Amount of foreign salt*	*Theoretical titration ml 0.1 N NaOH*	*Actual titration ml 0.1 N NaOH*	*NH_4CNS titration ml 0.1 N*
—	—	25.00	24.98	37.40
—	—	25.00	25.00	37.42
—	—	25.00	25.00	37.42
$NaBO_2$	25 ml 0.1 *M*	25.00	24.98	37.42
$NaBO_2$	25 ml 0.1 *M*	25.00	25.00	37.40
$NaBO_2$	25 ml 0.1 *M*	25.00	25.00	37.42
Na_2SO_4	5 g	25.00	25.00	—
Na_2SO_4	5 g	25.00	25.00	—
Na_2SO_4	5 g	25.00	25.01	—
A.A.S.	0.1 g	25.00	24.53	—
Na_2SiO_3	0.2 g	25.00	25.00	—
Na_2SiO_3	0.2 g	25.00	24.98	—
Na_2SiO_3	0.2 g	25.00	25.00	—

phosphate there was a small difference, the titrations without ammonium nitrate being slightly higher. The greatest difference was in the titration of a 50-ml aliquot, where duplicate sets disagreed by 0.24 and 0.27 ml respectively. A blank was run on 50 ml of the 0.1 *N* sodium hydroxide without ammonium nitrate and gave a titration of 0.19 ml. This is attributed to traces of carbonate in the alkali. A similar blank with ammonium nitrate gave a titration of less than 0.02 ml. The figures in Table V are corrected for these blanks.

A further seven titrations were done using 0.5 *M* phosphate to which sodium borate, sulphate and silicate were added. The results of this test are shown in Table VI.

It was concluded that even in the presence of other salts the omission of ammonium nitrate made a negligible difference to the result.

Halides interfere only by preferentially precipitating silver. The remedy is to add additional silver nitrate solution equivalent to the halide present.

TABLE V

COMPARISON OF EXPERIMENTS WITH AND WITHOUT AMMONIUM NITRATE

0.5 M Na_2HPO_4			*0.05 M Na_2HPO_4*		
Volume taken, ml	*Titration with NH_4NO_3, ml*	*Titration without NH_4NO_3, ml*	*Volume taken, ml*	*Titration with NH_4NO_3, ml*	*Titration without NH_4NO_3, ml*
10	9.82	9.82	10	9.84	9.84
10	9.80	9.83	10	9.80	9.85
25	24.50	24.56	25	24.55	24.49
25	24.49	24.51	25	24.50	24.49
50	48.85	49.00	50	49.01	49.06
50	48.78	49.02	50	48.96	49.04

TABLE VI

EFFECT OF OTHER SALTS ON TITRATIONS WITHOUT AMMONIUM NITRATE

Foreign salt	*Amount of foreign salt*	*Amount of 0.5 M phosphate (ml)*	*Theoretical titration (ml N NaOH)*	*Actual titration (ml N NaOH)*
$NaBO_2$	10 ml 0.1 *M*	10	9.82	9.86
$NaBO_2$	10 ml 0.1 *M*	10	9.82	9.85
$NaBO_2$	10 ml 0.1 *M*	10	9.82	9.87
Na_2SO_4	50 g	25	24.57	24.62
Na_2SO_4	20 g	25	24.57	24.55
Na_2SiO_3	1 g	25	24.57	24.50
Na_2SiO_3	1 g	25	24.57	24.58

EFFECT OF SURFACE ACTIVE MATTER

It will be obvious from the results in Tables I, II and IV that the presence of sodium alkylarylsulphonate completely vitiates the determination of phosphate. A set of experiments was done to attempt to establish a tolerance level for this material. In all experiments 25 ml of 0.05% *M* phosphate, 100 ml of water and 10 ml of 10% silver nitrate were used. Successively increasing amounts of 1% sodium alkylarylsulphonate solution were added and the results noted. In the absence of ammonium nitrate up to 0.02 g of the surface active material made no significant difference. With 0.03 g the error was only 0.12 ml. With 0.04 g the error was 0.45 ml and became rapidly greater with increasing contamination, reaching 4.4 ml with 0.1 g of surface active matter. All these erroneous results were too high.

With 1 ml of 20% ammonium nitrate there was again no error up to 0.02 g of contamination. The error then increased rather more rapidly than before, reaching 5.8 ml with 0.1 g of surface active matter. All these erroneous results were too low.

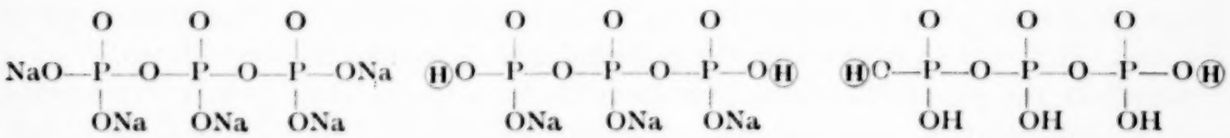
It appears that up to about 0.03 g of sodium alkylarylsulphonate, *i.e.* about 0.02% at the end of the titration, can be tolerated, whether or not ammonium nitrate is used.

The difference between the series with and without ammonium nitrate is very striking. It seems likely that without ammonium nitrate there is a limit to the proportion of silver phosphate which will be precipitated in the presence of surface active

matter, and that this limit is reached at a pH somewhere between 4.8 and 6.0. Beyond this point further additions of alkali cause precipitation of silver hydroxide. Thus the rate of increase of pH with addition of alkali is very slow and the final result is too high. Both the slow change of pH and darkening due to the formation of silver hydroxide were observed during the experiments. In the experiments with ammonium nitrate this limit would not be reached. Consequently at pH 4.8 the liberated acid has been completely titrated, but the phosphate is incompletely precipitated (less completely in fact than in the other series) and the titration is therefore too low. The precise mechanism of this phenomenon is not understood, but it is reasonable to expect surface active substances to interfere in some way with the mechanism of flocculation of the initially colloidal silver phosphate.

DETERMINATION OF MEAN CHAIN LENGTH OF CONDENSED PHOSPHATES

"Chain length" is used here to mean number of phosphorus atoms per molecule. Straight-chain condensed phosphates have the general formula $Na_{n+2}P_nO_{3n+1}$, arranged in structures analogous to those shown below for triphosphate[15].



pentasodium triphosphate

I

trisodium dihydrogen triphosphate (*i.e.* diacid form)

II

triphosphoric acid

III

The ringed hydrogen atoms in II and III are weakly acidic and may be titrated between pH values of 3.8 and 9.7 (for triphosphate; the corresponding values for other condensed phosphates decrease with increasing chain length). The remaining hydrogen ions in III are strongly acidic and are neutralised at pH 3.8. All straight-chain condensed acids have one strongly acidic hydrogen ion per phosphorus atom and one weakly acidic hydrogen atom at each end of the molecule.

VAN WAZER AND HOLST[16] determined the chain length of these substances by passing them through acid cation exchange resins to produce the free condensed acids, and plotting complete titration curves for these. All the curves showed two "steps", one at pH 3.5–4.0 and the other at pH 9–10. If V_1 ml is the volume required for the strongly acid hydrogen (*i.e.* the titration to the first "step") and V_2 ml the volume required by the weakly acid hydrogen (*i.e.* the titration between the two "steps") then $V_1/V_2 = n/2$ where n is the number of phosphorus atoms per molecule.

QUIMBY[17] determined the weakly acid hydrogen in the same way but calculated the number of strongly acid hydrogen ions from the total P_2O_5.

The method previously described for total P_2O_5 can also be used to determine the chain length of condensed phosphates. Such salts are converted to the diacid form $Na_nH_2P_nO_{3n+1}$ (analogous to II) by adjusting the pH to the value corresponding to the point of inflexion at the lower step of the titration curve. If the diacid form is treated with silver nitrate it reacts thus:

$$Na_nH_2P_nO_{3n+1} + (n+2)\,AgNO_3 \rightarrow Ag_{n+2}P_nO_{3n+1}\downarrow + n\,NaNO_3 + 2\,HNO_3$$

Each molecule thus yields two equivalents of hydrogen ion. If the phosphate is hydrolysed to the ortho-acid and analysed similarly, each molecule will yield n molecules of ortho-acid and therefore $2n$ hydrogen ions.

If these two experiments are performed on equal aliquots of the same solution, the mean chain length $\bar{n}$ is given by the ratio of the two titrations.

Procedure

Take a sample of condensed phosphate containing about 1 g of P_2O_5. It is satisfactory to assume the formula $(NaPO_3)_n$ in calculating the sample weight. Dissolve the sample in water, transfer it to a 250-ml volumetric flask and dilute to volume.

Place a 25-ml portion in a boiling flask, add 25 ml of 3 N nitric acid and boil gently under a reflux condenser for at least 30 min. Cool, transfer to a beaker and adjust the pH to 4.5. Add 10 ml of 10% silver nitrate solution and titrate to pH 6.0 with 0.1 N sodium hydroxide. Let this volume be V_2 ml.

While the first aliquot is boiling place a second 25-ml portion in a 250-ml beaker. Add 3 N nitric acid dropwise until the pH is about 3. Titrate slowly with 0.1 N sodium hydroxide, plotting pH against volume of alkali. Stop titrating as soon as a complete "step" has been plotted. From the graph determine the pH at which the slope is greatest. This is the pH at which the phosphate is present in its diacid form.

Readjust the pH to the value just determined, add 10 ml of 10% silver nitrate solution and titrate to pH 6.0 with 0.1 N sodium hydroxide. Let this volume be V_1 ml.

Mean chain length $\bar{n} = V_2/V_1$.

Results

This procedure was tested on pure samples of tetrasodium pyrophosphate, pentasodium triphosphate and hexaguanidinium tetraphosphate. The values found for the number of phosphorus atoms per molecule were 2.00, 3.02 and 4.00 respectively.

The diacid form of orthophosphate has a pH of 4.5. That of pyrophosphate is 4.2, and of triphosphate 3.8. For $n > 3$ the pH of the diacid form approaches a limiting value of about 3.5. Consequently mixtures of phosphates give less well-defined points of inflexion in their titration curves than single chemical entities, and even at the steepest point there will be some molecules present with too many hydrogen atoms and some with too few. (This is why the method of GERBER AND MILES[8] for orthophosphate in condensed phosphate is not entirely satisfactory; it is impossible simultaneously to have orthophosphate present exclusively as Na_2HPO_4 and pyro- and triphosphate present exclusively as $Na_4P_2O_7$ and $Na_5P_3O_{10}$ respectively). The resultant errors will, however, tend to cancel each other, as was shown by a test on a phosphate mixture recovered from a detergent powder. The method described gave a value for $\bar{n}$ of 2.66. The phosphate was analysed by ion exchange chromatography and a value for $\bar{n}$ calculated from the determined composition. It was 2.67.

This method of analysis may be regarded as a useful complement to the determination of total P_2O_5 on the one hand and the various chromatographic methods for determining the component phosphates on the other.

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SUMMARY

A method has been developed for the volumetric determination of orthophosphate, and a simple variation permits the determination of the average number of phosphorus atoms per molecule in condensed phosphates. For total P_2O_5 the phosphates are converted to the diacid ortho-salt and precipitated as silver phosphate. The liberated acid is then titrated. For determination of chain length the condensed phosphate is converted to the diacid form and treated similarly, then hydrolysed and determined as orthophosphate. The ratio of the two titrations is equal to the average number of phosphorus atoms per molecule.

RÉSUMÉ

Une méthode a été mise au point pour le dosage volumétrique des phosphates. Le phosphate (sous forme de MH_2PO_4) est précipité par le nitrate d'argent; l'acide libéré est titré par l'hydroxyde de sodium. Un procédé est également décrit pour l'analyse des polyphosphates.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur volumétrischen Bestimmung von Phosphaten. Das Phosphat (als MeH_2PO_4) wird mit Silbernitrat gefällt und die dabei entstehende Säure titriert. In modifizierter Form kann die Methode auch zur Bestimmung der Kettenlänge kondensierter Phosphate verwendet werden.

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CATALYSTS FOR CERIUM(IV) OXIDIMETRY

DETERMINATION OF PHOSPHITE, HYPOPHOSPHITE, TELLURIUM AND MERCURY

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In a previous paper[1] a new catalyst system was developed, which would extend the scope of cerium(IV) oxidimetry by providing a simple, rapid method for the determination of many difficultly oxidizable inorganic and organic compounds. This method, which involves the use of silver(I) and manganese(II) salts as catalysts in conjunction with a perchloric acid solution of cerium(IV) sulfate, has been applied to the determination of mercury(I)[1], and to the evaluation of hydroxyorganic compounds as glycerol, erythritol, and 8-quinolinol[2].

Volumetric methods for phosphite and/or hypophosphite are oxidation by bromate[3], iodine[4], hypobromite[5], and vanadate[6]. Procedures for tellurium include reduction to the metal and corresponding oxidation with iodine[7]; and periodate[8] and dichromate[9] oxidation of tellurium(IV).

Many of these methods require either strict control of experimental conditions or heating for prolonged periods to achieve satisfactory results.

RAO AND RAO[10] have proposed a catalytic oxidation of phosphite and hypophosphite with cerium(IV) sulfate, using silver sulfate, and WILLARD AND YOUNG[11] used chromium(III) sulfate to catalyze the ceric oxidation of tellurous acid. However time of reaction was still approximately 30 min in each instance.

Preliminary observations have shown that this new catalyst system greatly increases the rate of these reactions, thus providing a rapid method for the determination of these substances. Also a direct titration of mercury(I) is proposed using ceric perchlorate reagent, thus eliminating the necessity of back titration.

EXPERIMENTAL

All solutions were prepared from reagent grade chemicals and distilled water.

Cerium(IV) reagent, iron(II) solution, and mercury(I) perchlorate solution

All solutions 0.025 *F*, were described in a previous paper[1].

Ceric perchlorate solution

55 g of $(NH_4)_2Ce(NO_3)_6$ (G. F. Smith Chemical Co.) were added to 340 ml of 72% perchloric acid with stirring. The resulting solution was diluted to 1 l with water,

and transferred to a dark reagent bottle, covered with black insulating tape. This reagent was standardized every two weeks against arsenious acid.

Catalyst solution (A)

2.8 ml of 50% manganese(II) nitrate solution (J. T. Baker Chemical Co.) and 3.0 g of silver(I) nitrate were dissolved in 250 ml of 1 *F* perchloric acid.

Catalyst solution (B)

1.2 ml of 50% manganese(II) nitrate solution and 5.0 g of silver(I) nitrate were dissolved in 100 ml of 1 *F* perchloric acid.

Phosphite and hypophosphite solutions

These solutions were prepared by dissolving 1.909 and 0.530 g of the reagent grade sodium salts (Fischer Scientific Co.) in 1 l of distilled water, respectively, and were standardized according to the method of RAO AND RAO[10].

Tellurium solution

1.0 g of tellurium oxide was dissolved (Fischer Scientific Co.) in 20 ml of conc. HCl. The resulting solution was boiled down with 55 ml of 16 *M* sulfuric acid, diluted to 1 l, and standardized by the procedure of WILLARD AND YOUNG[11].

RECOMMENDED PROCEDURES

Determination of phosphite and hypophosphite

To a solution containing 10–100 mg of phosphite or 5–35 mg of hypophosphite, add 2 ml of catalyst solution (B), 5.5 ml of conc. sulfuric acid per each 100 ml of solution, and a 70–150% excess of cerium(IV). Heat on a hot plate, preset on high (or 100°) for 7 min in the case of hypophosphite and 10 min for phosphite. Quench the reaction by cooling and addition of 10 ml of conc. sulfuric acid, and titrate with standard iron(II) solution, using ferroin indicator.

Determination of tellurium(IV)

Heat a mixture containing 5–60 mg of tellurium, 1 ml of catalyst solution (A), 17 ml of 72% perchloric acid per each 100 ml of solution, and a 50–150% excess of cerium(IV) reagent on a hot plate at 95° until the solution rapidly turns cherry red in color. Quickly quench the reaction and proceed as described in the determination of phosphite.

The solution may be brown at the start of oxidation, but will gradually turn light yellow, and then red at the end-point. The reaction time is 3–7 min for 5–60 mg samples of tellurium. For best results the solution should not be boiled, nor heated past the formation of the cherry red color of permanganate. Because a small, nearly constant amount of oxidant is lost in the production of the red color, a blank correction should be applied (about 0.005 mequiv.). This may be determined by following the recommended procedure, but omitting the tellurium. The red color will appear upon heating. The difference between the mequiv. of iron(II) solution required for back titration and the number of mequiv. of cerium(IV) actually present represents the blank correction.

Determination of mercury(I)

Heat a solution containing 50–400 mg of mercury(I), 17 ml of 72% perchloric acid per each 100 ml of solution, and 1 ml of catalyst solution (A) to boiling. Immediately titrate with the ceric perchlorate solution, stirring continuously, to almost the end-point (which is the first permanent yellow color). Cool to 50–60°, add 2 drops of nitroferroin indicator, and continue the titration until the red color of the indicator disappears. If the end-point has already been passed, back titrate with standard iron(II) solution to the first tinge of pink.

DISCUSSION

Phosphite and hypophosphite

Due to the formation of insoluble cerium phosphite and phosphate in perchloric acid solutions, it proved impossible to use this acid media. Although reaction is much slower and the red end-point is not obtained in sulfuric acid solution, precipitation does not occur, and reaction proceeds smoothly. A 1.0-*F* sulfuric acid concentration proved optimum in both cases.

The amount of catalyst in solution (B) proved to be optimum for both determinations, reaction proving too slow and sluggish with catalyst (A). For best results in each determination, the per cent excess cerium(IV) reagent should be above 50% (Table I). Below this, incomplete oxidation occurs, causing low results.

TABLE I

EFFECT OF PER CENT EXCESS CERIUM(IV) REAGENT

Excess cerium(IV) %	Na_2HPO_3, *mg*		NaH_2PO_2, *mg*		*Tellurium, mg*	
	Present	*Found*	*Present*	*Found*	*Present*	*Found*
30.0	—	—	—	—	53.00	53.40
50.0	85.91	85.10	26.50	26.35	53.00	53.19
75.0	85.91	85.84	26.50	26.45	53.00	52.87
100.0	85.91	85.89	26.50	26.60	53.00	52.84
150.0	85.91	86.07	26.50	26.60	53.00	52.99

Heating periods of 7 and 10 min were found to be sufficient for all samples of hypophosphite and phosphite analyzed. However, the solution could be heated for one hour without error (Table II).

TABLE II

EFFECT OF OVERHEATING ON PHOSPHITE DETERMINATION

Time of reaction min	Na_2HPO_3, *mg*	
	Present	*Found*
10.0	85.95	85.99
15.0	85.95	85.99
30.0	85.95	85.99
60.0	85.95	85.99

The amount of each material may be calculated as follows:

$$\text{mg } Na_2HPO_3 = \frac{\text{mol. wt.}}{2} \text{ [net mequiv. of cerium(IV)]}$$

$$\text{mg } NaH_2PO_2 = \frac{\text{mol. wt.}}{4} \text{ [net mequiv. of cerium(IV)]}$$

Tellurium

Indication of the point of complete oxidation of tellurium(IV) depends upon the amount of excess cerium(IV) present. When 50% or more excess cerium is available, oxidation of the manganese catalyst to the cherry red of permanganate occurs at the point of complete oxidation. However the turbidity of manganese(IV) oxide does not occur at the equivalence point when the cerium(IV) reagent is below 50% excess as in the mercury(I) determination described previously[1], and the percent excess cerium(IV) should be above 50% for best results (Table I).

A 2.0-*F* perchloric acid concentration was found to be optimum. In 1.0-*F* acid the cherry red color does not readily appear, whereas in concentrations above 2.0-*F* there is additional error due to decomposition of excess cerium(IV) reagent by the catalysts.

RESULTS

Results of the determinations of phosphite, hypophosphite, tellurium(IV), and mercury(I) are shown in Table III. Samples of Na_2HPO_3 and NaH_2PO_2 ranging from 15–100 mg and 5–32 mg were evaluated with standard deviations of ±0.17 and

TABLE III

DETERMINATION OF PHOSPHITE, HYPOPHOSPHITE, TELLURIUM AND MERCURY

Na_2HPO_3, mg		NaH_2PO_2, mg		Error, %	
Present	*Found*	*Present*	*Found*	*Phosphite*	*Hypophosphite*
15.27	15.30	5.300	5.318	+0.19	+0.34
19.09	19.15	10.60	10.63	+0.31	+0.28
38.18	38.25	15.90	15.86	+0.18	−0.25
57.27	57.37	21.20	21.13	+0.17	−0.33
85.91	85.99	26.50	26.60	+0.093	+0.38
85.91	85.89	29.50	29.63	−0.023	+0.47
95.45	95.35	31.80	31.70	−0.10	−0.31
				$\sigma = \pm 0.17$	$\sigma = \pm 0.32$

Tellurium, mg		*Mercury, mg*		*Error, %*	
Present	*Found*	*Present*	*Found*	*Tellurium*	*Mercury*
10.40	10.42	67.80	68.20	+0.19	+0.49
21.20	21.24	90.00	89.90	+0.18	−0.11
39.75	39.84	113.0	113.8	+0.25	+0.70
53.00	52.99	158.2	158.3	−0.019	+0.068
69.62	69.80	253.6	252.0	+0.24	−0.60
84.10	84.34	355.0	354.3	+0.28	−0.18
106.0	105.7	507.0	505.0	−0.30	−0.38
				$\sigma = \pm 0.21$	$\sigma = \pm 0.36$

±0.32% respectively. 10–106 mg samples of tellurium(IV) were determined, using the red color of permanganate as end-point indication, with a standard deviation of ±0.21%.

Finally, 65–500-mg samples of mercury(I) were analyzed with a deviation of

$\pm 0.36\%$. These results may be compared to the indirect determination of mercury(I) in a previous paper, in which standard deviations of ± 0.22 and $\pm 0.32\%$ were obtained using the red permanganate color and the formation of manganese(IV) oxide as end-point indications[1]. The advantage of direct titration with ceric perchlorate solution is compensated by the disadvantage that ceric perchlorate is unstable, and must be restandardized every two weeks. The results by each method are comparable.

A photometric titration of mercury(I) with ceric perchlorate was attempted at 410 mμ, using the same conditions as described above. Samples ranging from 65–160 mg of mercury(I) were analyzed with a deviation of about $\pm 0.5\%$. Results were, in general, not as good as in the described procedure.

The presence of possible interferences in all determinations was studied briefly. All organic and inorganic substances oxidized by ceric under these conditions will interfere.

There is no differentiation of phosphite and hypophosphite possible under these catalytic conditions. If mixtures are to be determined, hypophosphite alone may be analyzed using the method of BERNHARDT[12], and then both substances determined catalytically.

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SUMMARY

A new catalytic oxidation procedure, involving the use of a cerium(IV) sulfate reagent in perchloric acid with a mixed silver(I)–manganese(II) perchlorate catalyst, has been developed for the determination of phosphite, hypophosphite, and tellurium. By this method 15–100 mg of phosphite, 5–35 mg of hypophosphite, and 10–105 mg of tellurium may be determined with standard deviations of ± 0.17, ± 0.32, and $\pm 0.21\%$ respectively. A direct titration procedure for mercury(I) is described using a ceric perchlorate solution as titrant with the mixed catalyst system. Samples from 65–510 mg may be analyzed with a standard deviation of $\pm 0.36\%$.

RÉSUMÉ

Un nouveau procédé est proposé pour le dosage des phosphites, des hypophosphites et du tellure, au moyen de sulfate de cérium(IV), en solution perchlorique. On utilise comme catalyseur un mélange de perchlorate d'argent(I) et de manganèse(II). Un titrage est également décrit pour le dosage du mercure(I).

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Phosphit, Hypophosphit und Tellur mit Hilfe von Cer(IV)-sulfat in perchlorsaurer Lösung in Gegenwart eines Katalysators (Mischung von Silber- und Mangan(II)-perchlorat). Nach dieser Methode kann auch Quecksilber(I) bestimmt werden.

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A COMPLEXOMETRIC TITRATION OF INORGANIC SULPHATE IN SYNTHETIC DETERGENTS

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A well-known method for the determination of sodium sulphate in synthetic detergents is to extract organic compounds with the aid of alcohol[1] or of 1 : 1 acetone–ethyl ether[2] and to determine the sodium sulphate as barium sulphate. When, however, the anionic detergent is a triethanolamine salt instead of a sodium salt this method fails, because triethanolamine sulphate is soluble in alcohol and the residue of the extraction with 1 : 1 acetone–ethyl ether is not crystalline. Moreover, the sodium salts of some alkyl ether sulphates do not readily dissolve in 1 : 1 acetone–ethyl ether, so that a quantitative separation from organic material, if at all possible, is very difficult to effect.

The purpose of this work was to overcome the above-mentioned difficulties and to find a rapid titrimetric method which avoids the time-consuming separation of sodium sulphate from the anionic active ingredient by solvent extraction. We found that the indirect titration of inorganic sulphate according to ANDEREGG *et al.*[3] cannot be used to determine sulphate in synthetic detergents owing to the interference of anionic surface-active agents, although the results are very good when no anionic synthetic detergents are present. A sharp end-point is reached also if the anionic synthetic detergent solution contains no sulphate and all the added barium is bound quantitatively by EDTA (See Table I). However, the values obtained by this titrimetric method for the recovery of added sulphate from sulphate-free anionic detergents were too low.

At first we supposed that the barium sulphate was not quantitatively precipitated, because insufficient barium chloride was present to precipitate both sulphate and lauryl sulphate as their barium salts. However, addition of an excess of barium chloride still gave low results. Sometimes the colour change was very sluggish.

SIJDERIUS[4] also obtained low results when the excess barium chloride was titrated immediately after boiling for some seconds and cooling. We therefore titrated sulphate in the presence of an anionic surface-active agent 24 h after boiling and cooling, but again obtained low results. If, after precipitation of sulphate as barium sulphate, lauryl sulphate was added, variable values were found depending on the time elapsed after precipitation. When lauryl sulphate was added immediately after precipitation low values were always obtained. Therefore we suppose that the barium sulphate is solubilised by the anionic detergent. The cationic surface-active agent cetyl pyridinium chloride (C.P.C.) does not interfere in the titration of sulphate, hence we tried

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to bind the anionic surface-active agent as a salt with this cationic agent and thus we succeeded in eliminating the solubilising action.

As the solution of C.P.C. and Eriochrome Black T has itself a blue colour, the latter compound cannot be used as indicator in this method. We did not check whether sulphate can be titrated in this manner in the presence of other cationic surface-active agents.

METHOD

Reagents

EDTA solution, 0.01 *M*: Dissolve 3.721 g disodium ethylenediaminetetraacetate dihydrate in 1 l of distilled water. Barium chloride solution, approximately 0.01 *M*: Dissolve 2.443 g barium chloride (A.R. grade), $BaCl_2 \cdot 2\,H_2O$, in distilled water and dilute to 1 l (Note 1). Cetyl pyridinium chloride, $C_{16}H_{33} \cdot C_5H_5N \cdot Cl \cdot H_2O$. (Pharmaceutical grade from Leda Chemicals Ltd., London). Indicator: Dissolve 0.09 g Metalphthalein (Phthalein Purpur obtained from Riedel-de Haën A.G., Seelze-Hannover) and 0.005 g Naphthol Green B in 0.5–1 ml aqueous ammonia (25%) and dilute with distilled water to 50 ml. This aqueous indicator solution is stable for one week (Note 2).

Procedure

Weigh a sample which contains approximately 0.02 g of sulphate, transfer to a 250-ml glass beaker and dissolve in 40 ml of distilled water. Add a small excess of C.P.C. (The requisite amount of C.P.C. can be determined by cationic titration of the anionic detergent according to EPTON[5] and WIJGA[6]). Acidify with 2 ml of 0.5 *N* hydrochloric acid and add 25 ml of the 0.01 *M* barium chloride solution. Heat and boil gently for 1–2 min. After cooling add 2 ml of indicator solution and 7.5 ml of aqueous 25% ammonia (Note 3). Titrate rapidly — to prevent formation of barium carbonate — with the 0.01 *M* EDTA solution. After the end-point has been reached add a small excess of the EDTA solution (Note 4). Add 100 ml of 96% ethanol and titrate with the barium chloride solution to a colour change from pale green to pale violet (Note 5).

Calculation

$$\frac{[(25 + a)t - 0.01\,b] \cdot 96 \cdot 100}{c} = d$$

a = ml of approximately 0.01 *M* barium chloride solution required for back-titration
t = molarity of barium chloride solution
b = ml of 0.01 *M* EDTA solution required for titration
c = mg of sample
d = percentage of sulphate ions in the sample.

Notes

1. The barium chloride solution must be standardized by the following procedure: Weigh approximately 550 mg of A.R. grade sodium sulphate, transfer to a 250-ml volumetric flask and dilute with water to 250 ml. Pipette 10 ml of the solution and titrate according to the described procedure without adding C.P.C.
2. If the end-point is not sharp, the indicator solution must be renewed.
3. The best results are obtained at a pH of approximately 11.

4. Sometimes only a change in colour intensity takes place, or the change is not perceptible at all. If after the addition of alcohol the colour is violet, some more EDTA solution must be added.

5. The end-point is satisfactory and is always obtained correctly by experienced analysts. If the solution of the synthetic detergent is coloured, Naphthol Green B must be omitted from the indicator solution.

RESULTS AND DISCUSSION

Table I lists the titrations of barium with EDTA in anionic synthetic detergent solutions which contain no inorganic sulphate; no C.P.C. was added.

TABLE I

THE RECOVERY OF BARIUM FROM SULPHATE-FREE ANIONIC SYNTHETIC DETERGENTS

Anionic	*mg anionic*	*ml $BaCl_2$ 0.01 M added*	*ml EDTA 0.01 M found*
Sodium alkyl aryl sulphonate	247.4	25.84	25.88
	521.3	25.81	25.87
Dioctyl ester of sodium sulphosuccinic acid	266.0	25.66	25.74
	490.5	25.29	25.38
Sodium lauryl sulphate	248.8	26.23	26.26
	504.9	26.09	26.10
Oleic acid ester of sodium isethionate	291.8	26.40	26.46
	524.8	25.93	25.98
Sodium alkyl naphthalene sulphonate	237.9	25.66	25.74
	501.4	25.69	25.59
Sodium palmitate	263.0	25.88	25.07
	526.3	27.49	26.37

The difference between added and recovered barium is less than 0.1 ml of 0.01 *M* barium chloride solution except in the case of sodium palmitate when greater differences are caused by the insolubility of palmitic acid, which occludes barium palmitate.

From the determinations of sodium sulphate in a solution of sodium lauryl sulphate without the addition of C.P.C. the following results are mentioned: From a solution containing 20.02 mg of sodium sulphate and 100 mg of sodium lauryl sulphate in different experiments only 15.76, 14.45, 13.60, 15.43 and 14.40 mg of sodium sulphate were recovered if the quantity of barium chloride added (0.25 mmole) was insufficient to precipitate both sulphate and lauryl sulphate. With an excess of barium chloride (0.25 mmole), 19.84, 19.75, 19.04, 19.18 and 19.24 mg of sodium sulphate were found by titration of solutions containing 20.01 mg of sodium sulphate and 50 mg of sodium lauryl sulphate.

The results of the sulphate determinations in sodium lauryl ether sulphate solutions by the described method are presented in Table II.

The 95% confidence intervals are calculated from these data and are —0.11 to 0.00 and 25.03 to 25.13, respectively.

The results of a number of determinations performed according to the procedure described are shown in Table III.

TABLE II

THE DETERMINATION OF SULPHATE IN SODIUM LAURYL ETHER SULPHATE

Anionic + C.P.C.			*Anionic + C.P.C. + Na_2SO_4*		
Anionic mg	*C.P.C. mg*	*Na_2SO_4 found, mg Y*	*Anionic mg*	*C.P.C mg*	*Na_2SO_4 found, mg Y*
324.8	353.0	−0.06	257.3	258.8	25.03
582.6	613.6	−0.16	588.0	648.3	25.03
427.2	441.5	−0.10	355.0	363.8	25.21
803.0	805.9	−0.04	426.5	434.1	25.05
569.4	584.8	+0.03	573.5	640.1	25.05
332.1	350.6	+0.03	399.8	419.7	25.13
429.9	438.7	−0.03	349.6	397.1	25.11
226.6	245.9	−0.09	191.6	203.8	25.02
		$\bar{Y}$ = −0.05			$\bar{Y}$ = 25.08
Standard deviation		S = 0.07	Standard deviation		S = 0.07
Added Na_2SO_4, mg		nil	Added Na_2SO_4, mg		= 25.03

TABLE III

DETERMINATION OF SULPHATE IN VARIOUS ANIONIC SURFACE-ACTIVE AGENTS

Anionics	*n*[a]	*Na_2SO_4 added mg*	*Na_2SO_4, found mg, Y*	*S*[b]	*95% Confidence interval*
Sodium alkyl aryl sulphonate	7	nil	0.00	0.03	−0.03 – 0.03
	7	22.99	23.13	0.04	23.09 – 23.17
Dioctyl ester of sodium sulphosuccinic acid	8	nil	0.20%[e]	0.02	0.18 – 0.22%[e]
	7	10.49	10.50[d]	0.09	10.43 – 10.58[d]
	7	23.13	23.15[d]	0.10	23.05 – 23.24[d]
Sodium lauryl sulphate	9	nil	0.05	0.05	0.01 – 0.09[e]
	7	22.99	23.01	0.06	22.96 – 23.07[e]
Sodium lauryl ether sulphate (see Table II)	8	nil	−0.05	0.07	−0.11 – 0.00
	8	25.03	25.08	0.07	25.03 – 25.13
Oleic acid ester of sodium isethionate	7	nil	−0.11	0.06	−0.16 – −0.05[f]
	8	24.99	24.89	0.06	24.84 – 24.94
Sodium alkyl naphthalene sulphonate	8	nil	0.01	0.03	−0.02 – 0.03
	8	24.87	24.95	0.06	24.90 – 25.00
Sodium palmitate	4	nil	0.00	0.05	−0.07 – 0.07
	4	24.99	25.01	0.04	24.95 – 25.07

[a] Number of experiments
[b] Standard deviation
[c] % Na_2SO_4 in dioctyl ester of sodium sulphosuccinic acid
[d] Corrected for blank
[e] A heavy precipitate is formed after the addition of alcohol
[f] Indicator: Metalphthalein, colour change from yellow to orange; the solution of this anionic has a yellow colour.

In the experiments summarised in Table III 200–800 mg of anionic and corresponding amounts of C.P.C. were used. The anionics were freed from inorganic sulphate by

repeated extraction with absolute ethanol, etc. Only the dioctyl ester of sodium sulphosuccinic acid was not completely free from sulphate. The titrations without the addition of sodium sulphate and the use of different amounts of this anionic (300–670 mg) resulted in a percentage of 0.20% sodium sulphate. The masking effect of this anionic — inorganic sulphate is not quantitatively precipitated as barium sulphate — is demonstrated by the fact that the recovery of barium in the same sample without the addition of C.P.C. is nearly quantitative (See Table I).

The results indicate very good accuracy and reproducibility. An inorganic sulphate determination in duplicate by the described method is done within an hour.

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SUMMARY

An accurate method for the determination of inorganic sulphate in synthetic detergents has been developed. After addition of a cationic surface-active agent (cetyl pyridinium chloride) to an anionic detergent, sulphate can be determined by means of indirect titration with EDTA, using a mixture of Metalphthalein and Naphthol Green B as indicator.

RÉSUMÉ

Une méthode a été mise au point pour le dosage de sulfate dans des détergents synthétiques. On effectue un titrage indirect au moyen de l'acide éthylènediaminotétracétique, après addition de chlorure de baryum.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Sulfat in synthetischen Waschmitteln durch indirekte Titration mit Aethylendiaminotetraessigsäure nach Zugabe von Bariumchlorid.

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THERMOGRAVIMETRIC DETERMINATION OF MAGNESIUM, POTASSIUM AND LEAD BY PRECIPITATION WITH DILITURIC ACID

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INTRODUCTION

Dilituric acid (5-nitrobarbituric acid) was first prepared in 1845 by SCHLIEPER[1] and many of its salts shortly thereafter[1,2]. Despite the fact that this was about a hundred years ago, relatively little is known about them even today. The solubilities of a number of dilituric salts have been measured by REDEMANN AND NIEMANN[3]. Dilituric acid has been proposed for use as a precipitating agent for the determination of a number of cations and also for several organic bases[3-5]. DICK used dilituric acid for the determination of copper, cadmium, cobalt, and nickel[5] and DE GRAAFF AND NOYONS[6] reported a method for potassium. These methods offer the advantage of rapidity, accuracy and favorable gravimetric factor but suffer from the lack of specificity.

Methods for the determination of magnesium and potassium have been developed by us and the determination of lead has also been investigated. Thermolysis curves have been established for these precipitates to ascertain their compositions and thermal stabilities. The thermolysis curve for $MgNH_4PO_4 \cdot 6H_2O$ has also been traced since the magnesium solution used in these determinations was standardized by precipitation as $MgNH_4PO_4 \cdot 6H_2O$ and it was thought desirable to investigate the thermal conditions for the conversion of $MgNH_4PO_4 \cdot 6H_2O$ to $Mg_2P_2O_7$.

THERMOLYSIS CURVES

Many complexes and salts which have been proposed for the gravimetric determination of metallic cations suffer from a lack of thermal stability, rendering their use problematic in many cases. For example, $Mg(NH_4)_2Fe(CN)_6$ proposed by FEIGL AND PAVELKA[7] for the determination of magnesium is unstable above 50°. As a further example ZAN'KO AND BURSUK[8] recommend drying lead dibromo-5,7-oxinate at 195° to 215° in a proposed quantitative method but it has been shown by its thermolysis curve that it does not correspond to this composition[9].

The thermolysis curves for magnesium, potassium and lead dilituratates have been obtained to investigate the quantitative utility of these compounds. The thermolysis curves for magnesium, potassium and lead dilituratate show that their stabilities are quite adequate for their utilization in gravimetric determinations.

Experimental

Equipment

An ADAMEL recording thermobalance (Chevenard System) was used to obtain the thermolysis curves.

Salts of dilituric acid

Potassium dilituratc. A hot solution of saturated dilituric acid at 25° was added in excess to a solution of reagent grade potassium chloride in water. Anhydrous potassium dilituratc ($KC_4N_2H_2O_3 \cdot NO_2$) formed after a few minutes. The solution was cooled in an ice bath, and the precipitate was filtered, washed with water and dried at 100° for one hour.

Magnesium dilituratc octahydratc. A 0.02-*M* solution of Merck reagent grade magnesium sulfate was treated with an excess of saturated dilituric acid solution. The magnesium dilituratc octahydratc [$Mg(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 8H_2O$] precipitate was left to form for several hours, cooled, filtered, and washed twice with a 0.02% dilituric acid solution in 50% ethanol and finally with anhydrous ether.

Lead dilituratc dihydratc. Saturated dilituric acid was added to reagent grade lead nitrate in water. The solution was allowed to stand overnight. A compact crystalline deposit of lead dilituratc [$Pb(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 2H_2O$] formed. The crystals were filtered and washed with a water solution containing a small concentration of lead nitrate; they were then dried for one hour in an oven at 75°.

Carbon and hydrogen analyses of the above compounds are as follows:

	Calculated	*Analysed*
Potassium dilituratc		
$KC_4N_2H_2O_3 \cdot NO_2$	C: 22.75%; H: 0.96%	C: 23.27%; H: 1.15%
mol. wt. 211.18		C: 23.12%; H: 0.95%
Magnesium dilituratc octahydratc		
$Mg(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 8H_2O$	C: 18.74%; H: 3.94%	C: 19.24%; H: 3.93%
mol. wt. 512.64		C: 19.33%; H: 4.16%
Lead dilituratc dihydratc		
$Pb(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 2H_2O$	C: 16.36%; H: 1.38%	C: 16.76%; H: 1.32%
mol. wt. 587.43		C: 16.62%; H: 1.50%

Magnesium ammonium phosphate hexahydratc. This compound ($MgNH_4PO_4 \cdot 6H_2O$) was formed from a 0.0216-*M* solution of magnesium sulfate using the procedure of LUNDELL AND HOFFMAN[10].

Method

The thermolysis curves, Fig. 1, were obtained by heating the dilituratcs in No. 000 porcelain crucibles, while magnesium ammonium phosphate hexahydratc was heated in a No. 8, medium porosity, sintered glass filter. The weights of the samples and the corresponding rates of heating are given in Fig. 1. All the samples were heated in air with the exception of magnesium dilituratc which was run in dry nitrogen flowing at the rate of 2 l per hour.

Discussion

The thermolysis curve of potassium dilituratе has been determined previously by DUVAL[9]. He mentions that very little decomposition is observed before 400° while a mild explosion occurs towards 500°.

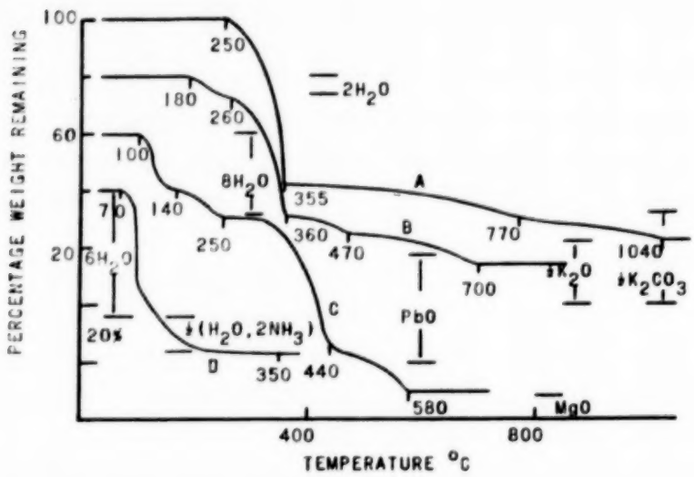

Fig. 1. Thermal decomposition curves of metal dilituratеs and of magnesium ammonium phosphate hexahydrate. A. Potassium dilituratе, 373.8 mg heated at 300°/h; B. Magnesium dilituratе octahydrate, 109.5 mg heated at 65°/h; C. Lead dilituratе dihydrate, 37.6 mg heated at 150°/h; D. Magnesium ammonium phosphate hexahydrate, 106.8 mg heated at 65°/h.

We have found that anhydrous potassium dilituratе was stable to 250° on heating, but decomposed rapidly between 250° and 355°. Above 355° there was a slow decomposition terminating at 1040° with the production of K_2O. At 770° there was an inflection point corresponding to the composition of K_2CO_3. Potassium dilituratе prepared by the same method but not dried previously in the oven gave the same type of thermolysis curve.

The dehydration of magnesium dilituratе octahydrate started at 100° and proceeded in two steps. An intermediate semistable hydrate was formed at 140°, after the loss of four molecules of water; after the loss of four additional molecules of water the anhydrous compound was obtained, stable between 220 and 260°. Above 260° there was a rapid but nonexplosive decomposition. An inflection point found at 440° corresponded to a weight 8% larger than would be the weight of $MgCO_3$. At 580° constant weight was obtained which was 11% of the original weight and corresponded to slightly more than the percentage weight of MgO. When an X-ray powder diffraction pattern was taken of the residue it gave only lines corresponding to MgO.

Lead dilituratе formed a compound stable to 180°. The decomposition which followed to 260° produced a loss in weight corresponding to two molecules of water. A subsequent fast decomposition occurred up to 370°; from there a slow decomposition took place to 700° with an inflection point at 470°. The weight at 470° corresponded to $PbCO_3$ and at 700° to PbO.

The thermal decomposition curve of magnesium ammonium phosphate hexahydrate has been described by DUVAL[9]. He gave 46° as the temperature at which dehydration begins and 477° as the temperature at which the total conversion to $Mg_2P_2O_7$ is reached. The heating rate used by DUVAL was 300°/h. In our experimental work with a heating rate of 65°/h the dehydration started at 40° and $Mg_2P_2O_7$ was obtained at 350°. An inflection point occurred after a loss corresponding to the weight of 6 H_2O or 5 molecules of water and one of ammonia. When a heating rate of 150°/h was used dehydration began at 80° and the decomposition was terminated at 420°. It is quite likely therefore that the higher temperature recommended by certain

authors for the pyrolysis of magnesium ammonium phosphate is necessary because of a fast rate of heating (above 1000°/h). As an explanation, under such conditions an impermeable coating of fused $Mg_2P_2O_7$ probably forms on the precipitate particles rendering difficult the subsequent escape of the remaining water and ammonia.

THERMOGRAVIMETRIC DETERMINATION OF MAGNESIUM WITH DILITURIC ACID

There are numerous methods for the determination of magnesium. When magnesium is present in concentrations larger than 0.02 *M* and with amounts larger than 10 mg, gravimetric, volumetric or complexometric methods are most suitable.

Among the best gravimetric methods for minimum amounts of magnesium is precipitation with tropeolin 00[11] or with 8-hydroxy-quinaldine[12]. The latter method permits a very good separation of magnesium from calcium and many other cations. When the amounts of magnesium are larger, the best gravimetric methods involve precipitation with 8-hydroxyquinoline[13] or with diammonium hydrogen phosphate[14]. The diammonium hydrogen phosphate method though frequently used is subject to a number of criticisms, namely slow precipitate formation, reprecipitation to improve purity of precipitate and time-consuming ignition to the pyrophosphate.

Since magnesium forms the most insoluble dilituratе thus far reported in the literature[3] it seemed to offer possibilities as a rapid and accurate method for the determination of magnesium.

Experimental

Solutions

Standard magnesium solution. This solution was prepared from recrystallized reagent-grade anhydrous magnesium sulfate, dried for two hours at 100°. The concentration was 0.524 mg of Mg/ml or 0.02164 *M*. The magnesium content of this solution was verified by analysis as the pyrophosphate (see discussion section) with a deviation of 2 p.p.m. from its concentration by weight. Since this is within the experimental error of the method the original standard value was used.

Dilituric acid solution. The dilituric acid solution was prepared by saturating a 50% ethanol solution with recrystallized dilituric acid trihydrate. Solution was accelerated by heating; the excess dilituric acid was filtered off after cooling. This solution was about 0.05 *M*.

Method of analysis

10-ml aliquots of the standard magnesium solution were treated with 25 ml of the dilituric acid solution. (Other volumes of magnesium were treated with proportionate volumes of reagent so that a molar ratio of D/Mg of about 5/1 was used). The magnesium dilituratе was left to form for no more than 30 min at room temperature. It was then cooled in ice and filtered on a glass fritted filter of medium porosity. The precipitate was washed with saturated dilituric acid solution and finally with 95% ethanol. For the thermogravimetric determination the sintered glass filter containing the precipitate was placed on the thermobalance, preheated to a temperature between 70 and 90°. Constant weight for the octahydrate was obtained in about 10 min. The heating cycle of the furnace was then started at 300°/h until a temperature of about 220° was reached, and the furnace then thermostated. The weight of the anhydrous precipitate was recorded. In this way two values for the amount of magnesium present were obtained.

Analytical results

Table I lists the results obtained by this method. The magnesium concentration in the above determinations was 0.526 mg/ml with the exception of 0.105 mg/ml for the 1-mg sample and 0.263 mg/ml for the 5-mg samples.

TABLE I

THERMOGRAVIMETRIC DETERMINATION OF MAGNESIUM AS DILITURATE

Ppt. (mg)	*Mg taken (mg)*	*Mg found (mg)*	*Dev. (mg)*
Weighed as $MgD_2 \cdot 8H_2O$			
22.4	1.05	1.06	+0.01
56.3	2.63	2.67	+0.04
56.6	2.63	2.68	+0.05
109.8	5.26	5.21	−0.05
109.6	5.26	5.20	−0.06
110.0	5.26	5.22	−0.04
109.9	5.26	5.21	−0.05
110.9	5.26	5.26	0.00
110.9	5.26	5.26	0.00
110.0	5.26	5.26	0.00
110.6	5.26	5.25	−0.01
546.4	26.32	25.92	−0.40
546.1	26.32	25.90	−0.42
Reweighed as MgD_2			
16.1	1.05	1.06	+0.01
41.4	2.63	2.73	+0.10
41.3	2.63	2.72	+0.09
79.4	5.26	5.24	−0.02
79.5	5.26	5.25	−0.01
79.4	5.26	5.24	−0.02
79.2	5.26	5.23	−0.03
80.4	5.26	5.31	+0.05
80.2	5.26	5.29	+0.03
79.7	5.26	5.26	0.00
79.9	5.26	5.27	+0.01
395.5	26.32	26.40	−0.22
394.1	26.32	26.01	−0.31

In Table II are listed the results showing the interference of calcium in the determination of magnesium as magnesium diliturate and in Table III are shown the effects of large dilution of the magnesium solution, very rapid dehydration of the octahydrate as well as the precipitation of magnesium diliturate in the presence of oxalate ions upon the magnesium results.

Discussion of results

The results for the determination of magnesium obtained in Table I are slightly lower than the primary standard values in the case of the larger amounts of magnesium (about 0.02 mg or 0.4% on the average). Solubility calculations indicate that under

our experimental conditions the maximum solubility of magnesium should be only $8 \cdot 10^{-6}$ mg. This is a negligible percentage loss of the total magnesium present.

When the concentration of magnesium was small (0.033 mg/ml) appreciable negative deviations (see Table III) were obtained. A solubility calculation similar to the one above indicates that the amount of magnesium left in solution should not exceed $7 \cdot 10^{-4}$ mg. This amount is too small to account for the increase in experimental error.

The standardization of the magnesium solution with pyrolysis of the magnesium ammonium phosphate in an electric muffle furnace at 1100° according to the

TABLE II

CALCIUM INTERFERENCE IN THE PRECIPITATION OF MAGNESIUM DILITURATE

Ca present (mg)	*Conc. Ca (mg/ml)*	*Excess Ppt. (mg)*	*Ca Pptd. (mg)*	*Time for Ppt. formation*
0.16	0.004	1.20	0.11	22 h
0.80	0.018	6.80	0.49	25 min
0.80	0.018	7.41	0.53	12 h

TABLE III

EFFECT OF CONCENTRATION, RATE OF HEATING AND OXALATE INTERFERENCE ON THE DETERMINATION OF MAGNESIUM AS MAGNESIUM DILITURATE OCTAHYDRATE

Conc. Mg taken (mg/ml)	*Weighed as $MgD_2 \cdot 8H_2O$*			*Reweighed as MgD_2*	
	Mg taken (mg)	*Mg found (mg)*	*Dev. (mg)*	*Mg found (mg)*	*Dev. (mg)*
0.263[a]	2.63	2.68	+0.05	2.72	+0.09
0.263[b]	2.63	2.67	+0.04	2.73	+0.10
0.033	5.26	5.05	−0.21	5.53	+0.27
0.088	5.26	5.19	−0.07	5.40	+0.14
0.263	5.26	5.20	−0.06	5.65	+0.39

The precipitates from the 5.26-mg samples of magnesium were dehydrated at a rate of heating above 700°/h.

[a] does not contain oxalate

[b] is 0.0269 *M* in respect to oxalate

LUNDELL AND HOFFMAN method gave an average of 0.5187 mg/ml of Mg. It is possible, as mentioned by them, that some decomposition of the precipitate occurred at that temperature.

With the modified procedure the precipitation was identical. The precipitate was filtered through a fritted glass filter. It was first dried at 70° in the thermobalance to obtain $MgNH_4PO_4 \cdot 6H_2O$ and then decomposed to $Mg_2P_2O_7$ by heating to 620° at the rate of 150°/h.

An average magnesium concentration of 0.5257 mg/ml was obtained from the hydrate and 0.5293 mg/ml from the $Mg_2P_2O_7$. This gives an overall average of 0.5275 mg/ml or a deviation of +2% from the value taken as standard.

In order to dehydrate magnesium diliturate octahydrate heating at a temperature of 220° is necessary. At 300°/h, the rate of heating normally used, it takes 45 min to

reach this temperature. Heating at 700°/h would shorten the heating time to less than 20 min but gave magnesium results about 6% above the weight of magnesium taken (see Table III). This probably is due to incomplete dehydration as in the pyrolysis of magnesium ammonium phosphate hexahydrate.

The determination of magnesium by precipitation with dilituric acid is not possible in the presence of calcium, since calcium interferes even at very low concentrations. A solubility calculation for our experimental conditions shows that the solubility product of calcium dilituratе is exceeded only when the concentration of calcium is in excess of 0.08 mg/ml. The highest concentration of calcium that we have used is 0.018 mg/ml (see Table III), which is well below the maximum allowable concentration according to the solubility calculation, but coprecipitation nevertheless takes place. In the two samples containing 0.80 mg of calcium the precipitates were left to form for 25 min in one case and for 12 h in the other. The amount of excess precipitate was independent of time. One can conclude that there is coprecipitation of calcium dilituratе on magnesium dilituratе and not postprecipitation.

The first two results in Table III show that concentrations of oxalate ion as high as 0.027 *M* do not interfere with the determination of magnesium. The amount of magnesium found was the same in both cases yet only the second sample contained oxalate ions. This would allow calcium if present in solution, to be separated as the oxalate before the subsequent determination of magnesium as dilituratе.

Amounts of magnesium ranging from 1 to 26 mg and with concentrations between 0.1 and 0.5 mg/ml can be determined by precipitation as magnesium dilituratе very rapidly and with an error less than 0.5%. The double determination of the hydrated and anhydrous forms allow for better accuracy and at the same time for detection of coprecipitated substances.

THERMOGRAVIMETRIC DETERMINATION OF POTASSIUM WITH DILITURIC ACID

The determination of potassium has always presented a problem since large solubility errors are characteristic of even the most widely used gravimetric methods. More recently colorimetric and spectrophotometric methods have been developed particularly suited for small samples. There is a definite need for an accurate gravimetric method.

When potassium is the only cation present in solution it can be determined as the chloride or the sulfate. The sulfate is also conveniently used for the determination of potassium in organic materials after digestion with sulfuric acid. A number of precipitating agents such as perchlorate, dipicrylaminate, chloroplatinate and 6-chloro-5-nitro-*m*-toluene sulfonate have been used for the determination of potassium in the presence of small amounts of other metals and alkalies, but in all these determinations caesium and rubidium are also coprecipitated[9].

Dilituric acid has also been used for the determination of potassium. FREDHOLM[4] used it for the qualitative microscopic detection. DE GRAAFF AND NOYONS[6] quantitatively determined potassium, weighing the precipitate after drying at 100°. Their results for quantities of potassium larger than 1 mg were too high while for amounts smaller than 1 mg were erratic. The maximum quantity determined by them was 2 mg. These authors have found that by washing the precipitate with saturated potassium dilituratе in 40% ethanol they could obtain values close to theoretical.

It was to examine the conditions of precipitation and to extend the range of po-

tassium concentrations determined that the authors undertook the determination of potassium with dilituric acid.

Experimental

Solutions

Standard potassium chloride solution. A standard solution was prepared from recrystallized reagent grade KCl dried for two hours at 110°. The potassium concentration was 2.148 mg/ml.

Trimethylamine dilituratе solution. As precipitating agent we first tried the dilituric acid solution used for the determination of magnesium, but when this solution proved too dilute we dissolved trimethylamine dilituratе in 50% ethanol until saturated. The excess trimethylamine dilituratе was filtered off. This solution had a pH of 7 and a concentration around 0.1 *M* or double that of the dilituric acid solution.

The trimethylamine dilituratе was prepared by adding an excess of saturated aqueous solution of dilituric acid to a 1- to 2-% aqueous solution of trimethylamine. The resulting mixture was heated until the precipitate dissolved, and then cooled slowly to 0°. Beautiful large green needles of trimethylamine dilituratе precipitated out of solution. They were filtered and dried in air.

Method of analysis

A 2-ml aliquot of the standard potassium solution was treated with 15 ml of hot trimethylamine dilituratе solution. The precipitate was left to form and cool for 1 to 2 h. About 20 min before filtration 5 ml of cold precipitating agent was added, the solution stirred and then cooled in an ice bath. The precipitate was filtered on a sintered glass crucible; once in the crucible it was washed with a saturated potassium dilituratе solution in 50% ethanol and finally once with 95% ethanol. The crucible was then placed on the thermobalance thermostated at a temperature ranging from 160° to 230°. The weight of the anhydrous precipitate was obtained within 15 to 20 min.

For different amounts of potassium, proportionate volumes of the trimethylamine dilituratе solution were added so as to have a 15- to 20-fold excess of trimethylamine dilituratе over potassium.

Results and discussion

In Table IV are results obtained with the above method. The effect of adding the precipitant in one or two portions is shown in Table V.

The trimethylamine dilituratе solution was used as the precipitant only after dilituric acid solution was found to be unsatisfactory. Excessively large volumes of the dilituric acid solution were necessary in order to obtain the desired excess of dilituratе ions over the potassium ions.

Satisfactory results were obtained only with neutral solutions of the precipitating agent. When the triethylamine dilituratе solution was made basic with an excess of trimethylamine the trimethylamine had a tendency to coprecipitate on the potassium salt; on the other hand, if the trimethylamine dilituratе solution was made acidic with hydrochloric acid there was incomplete precipitation.

The tendency of potassium dilituratе to supersaturate and to form very fine precipitates is very well avoided by two subsequent additions of the trimethylamine dilituratе precipitating solution (see Table V).

We have found experimentally from the thermogravimetric curves that 50 to 75 mg of liquid are retained by the filtering crucible (this is an objection to the method of DE GRAAFF where the precipitate was washed solely with saturated potassium dilituratе solution). The glass filter should be as small as possible so as to retain the minimum of wash solution even with a final washing with 95% ethanol.

TABLE IV

THERMOGRAVIMETRIC DETERMINATION OF POTASSIUM WITH DILITURIC ACID

K taken (mg)	*K found (mg)*	*Dev. (mg)*
4.29	4.50	+0.21
4.30	4.24	—0.06
3.22	3.16	—0.06
3.01	3.00	—0.01
3.44	3.66	+0.22
2.15	2.05	—0.10
2.15	2.09	—0.06
2.15	2.09	—0.06
2.58	2.25	—0.33
2.15	2.11	—0.04
2.58	2.33	—0.25
1.72	1.52	—0.20
1.72	1.55	—0.17
1.28	1.25	—0.03

TABLE V

METHOD OF PRECIPITATING POTASSIUM DILITURATE

K taken (mg)	*K found (mg)*	*Dev. (mg)*	*Portions of precipitant*
2.15	1.94	—0.21	1 addition
2.15	2.05	—0.10	2 additions
3.22	2.93	—0.29	1 addition
3.22	3.16	—0.06	2 additions

From the data in Table IV it can be seen that the results tend to be low. This method does not eliminate completely the effect of supersaturation, since from calculations on solubility data the negative error is greater than expected. Using the solubility data of REDEMANN AND NIEMANN[3] under our experimental conditions with a dilituratе ion concentration of 0.1 *M* and an initial concentration of potassium of 0.02 *M* there would be a negative error of 3%. This gives an error of —0.06 mg for a 2.15-mg sample of potassium. If this correction is made, twelve of the fifteen results have very good agreement with the weight of potassium taken.

We have studied the possibility of determining potassium in the presence of sodium but have found that sodium dilituratе coprecipitates even when present in small amounts in spite of the fact that the solubility of the sodium salt is 10 times that of the potassium salt.

Potassium can be determined by precipitation with dilituric acid in the absence

of sodium. Increased accuracy of results is obtained by applying an appropriate solubility correction for potassium dilituratе. A determination can be completed in about three hours with an error not exceeding 2%.

PRELIMINARY INVESTIGATION FOR THE THERMOGRAVIMETRIC DETERMINATION OF LEAD WITH DILITURIC ACID

The simplest and best known gravimetric method for the determination of lead weighs the lead as sulfate. The need to correct for the high solubility of lead sulfate, and to heat the precipitate to more than 300° plus an unfavorable gravimetric factor make the use of some other precipitate desirable particularly when the quantity of lead is small. HECHT and coworkers[15] recommend picrolonic acid in such cases. Lead picrolonate washes and filters well, is stable up to 112° but picrolonic acid is an expensive reagent.

It was thought that dilituric acid which is inexpensive would also have the favorable properties possessed by picrolonic acid.

Solutions

Standard lead solution. Recrystallized anhydrous lead nitrate dried in air was weighed, dissolved in water and diluted to volume to yield 0.02-*M* solutions.

Dilituric acid solution. A 0.02-*M* solution in 40% ethanol was prepared.

Method of analysis

Dilituric acid solution was slowly added to 25 ml of the 0.02-*M* lead nitrate solution until there was a 50% excess (molar) of dilituratе ions. The precipitate was digested for 30 min on a hot plate, and then left to form for several hours in an ice bath. It was then filtered through a sintered glass filter of medium porosity, washed several times with a 0.001-*M* solution of dilituric acid in 50% ethanol, and once with 95% ethanol. The glass filter and precipitate were heated in the thermobalance in an atmosphere of CO_2 at the rate of 150°/h and the anhydrous form between 180° and 200°/h.

Analytical results

The results, mostly of a preliminary nature, obtained with the above method are listed in Table VI. Some results obtained when the ratio of dilituratе to lead was only slightly above 1 are also recorded in Table VI.

TABLE VI

THERMOGRAVIMETRIC DETERMINATION OF LEAD AS ANHYDROUS LEAD DILITURATE

Pb taken (mg)	*Pb found (mg)*	*Dev. (mg)*
Molar ratio of dilituratе to lead 1.5/1.0		
42.6	42.3 (anhydrous)	−0.3
42.6	42.5 (anhydrous)	−0.1
51.1	52.1 (hydrate)	+1.0
51.1	52.2 (anhydrous)	+1.4
Molar ratio of dilituratе to lead 1.0/1.0		
53.1	49.7 (anhydrous)	−3.4
53.1	49.1 (anhydrous)	−4.0
53.1	49.6 (anhydrous)	−3.5

Discussion of results

Preliminary results using equimolar quantities of lead and dilituric acid gave negative deviations of about 4%. Assuming this is due to the solubility of lead dilituratе a K_{sp} value of $4 \cdot 10^{-4}$ was calculated in the 25% ethanol solution at 0°. This is a solubility of 1 mmole of lead dilituratе per l. In these calculations it is assumed that there is no supersaturation.

When the ratio of dilituratе to lead was increased to 1.5/1.0 the results had a deviation of somewhat less than —0.5%. Digestion of the samples improved the accuracy of the results, as is indicated by the 42.6-mg samples in Table VI.

In a preliminary experiment it was found that the presence of ethanol is essential, since otherwise the precipitate forms only very slowly and incompletely.

Dilituric acid can be used for determining semi-micro amounts of lead in a reasonably short time. One and a half hours for the precipitation and 30 min for the determination of the final weight on the thermobalance.

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SUMMARY

The thermolysis curves of magnesium, potassium, and lead dilituratе have established that either the hydrated or anhydrous forms of these precipitates are stable enough for their gravimetric use to be possible. Magnesium and lead were determined by precipitation with dilituric acid while potassium was precipitated with trimethylamine dilituratе.

RÉSUMÉ

Les courbes de thermolyse des dilituratеs de potassium, de magnésium et de plomb ont montré que ces composés sont suffisamment stables pour permettre un dosage gravimétrique de ces éléments.

ZUSAMMENFASSUNG

Der Verlauf der thermolytischen Kurven der Dilituratе von Kalium, Magnesium und Blei zeigt, dass diese Verbindungen sich zur gravimetrischen Bestimmung der erwähnten Elemente eignen.

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THE IDENTIFICATION OF ALIPHATIC AMINES IN AIR AS THEIR BENZAMIDES BY PAPER CHROMATOGRAPHY

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INTRODUCTION

As a portion of a program of the study of individual species in collections from polluted atmospheres, it was felt desirable to develop a method for the separation and identification of aliphatic amines. Several alternative methods were considered[1,2], but in view of experience in our laboratory[3] with the method of DE JONGE[4,5] it was decided that an investigation should be made of the possible use of the benzamides as suitable derivatives for paper chromatography. As has been previously noted[3], it is possible greatly to extend the lower limit of such a technique by the use of ^{14}C labelling.

PROCEDURE

Materials

Chemicals used, except where otherwise noted, were reagent grade, or the purest available. Benzoic acid, labelled with ^{14}C in the carboxyl group, was purchased from Tracer Laboratory. It had a nominal specific activity of 1.46 mC/mm. Benzoyl chloride was prepared from this in the usual way[6].

Lower molecular weight benzamides for calibration purposes were prepared by the SCHOTTEN-BAUMAN reaction[7]. The higher molecular weight derivatives were made by the method of SASIN *et al.*[8].

Schleicher and Schüll papers 2040a gl. and 2045a gl. were used as indicated for the paper chromatographs. Radioautographs were prepared using Eastman Kodak x-ray film, no screen.

DE JONGE's systems are as follows: System M: 80% methanol–cyclohexane; ratio 20:80; System P: 50% ethanol–cyclohexane, ratio 20:80; System E: 20% propanol–cyclohexane, ratio 20:80.

Determination of R_F values

A solution of each pure benzamide containing approximately 2 mg/ml was chromatographed according to the procedure of DE JONGE[4] at 20°. The spots were located in the usual fashion by means of ultraviolet light. The results are tabulated in Table I for DE JONGE's systems M and E. System P was also tried, but found unsatisfactory. Mixtures of benzamides containing approximately 2 mg/ml of each benzamide were found to separate adequately in most cases, as would be anticipated by the R_F values given.

Determination of lower limit of identification

For this purpose, very dilute solutions of the radiocarbon-type benzamides were chromatographed, placed on x-ray film for eight to ten days and the radioautographs developed in the usual way. The lower limit of identification was found to be approximately 2.5 μg of each benzamide. Quantitative measurements could be made on larger amounts by elution according to DE JONGE AND VERHAGE[5] and by a measurement of the absorbance at 225 mμ with a Beckman spectrophotometer, Model DU.

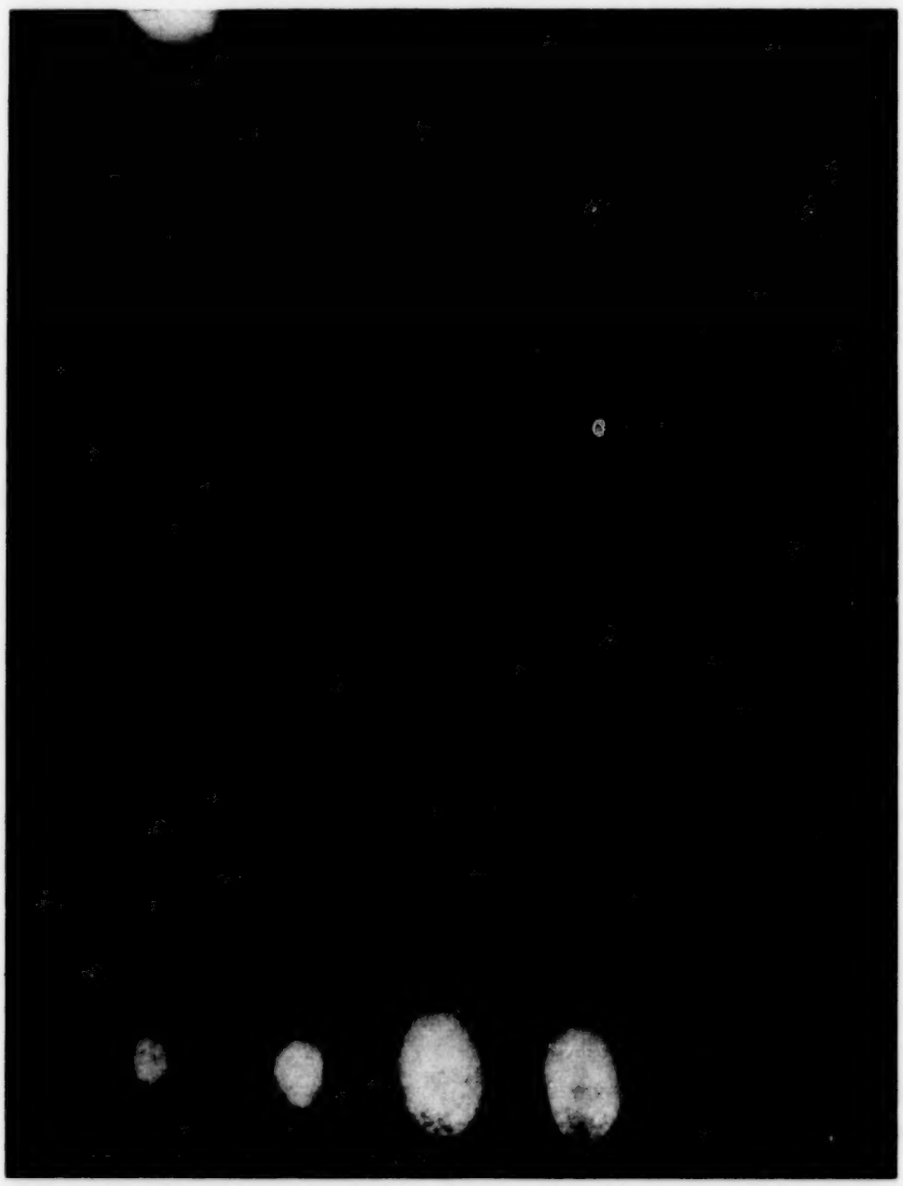

Fig. 1. Radioautograph illustrating separation of even straight chain mixtures of N-benzamides.

Preparation of air samples

Samples of airborne particulate matter collected on glass fiber filters were supplied by the National Air Sampling Network, U. S. Public Health Service. A quantity of filter bearing 3 to 8 g of particulate matter was chopped into small squares, dampened with sodium hydroxide, and extracted with three 250-ml portions of anhydrous

redistilled ether by shaking. Since it was found that all of the amines were removed from a mixture of amine salts in two ether extractions of 20 min each, by reacting the extract with benzoyl chloride, it was assumed that a total extraction time of 11–12 h with ether and sodium hydroxide was sufficient to remove any amines from the particulate matter. After this interval the extract was decanted through a filter and acidified with hydrogen chloride gas. The volume of extract was reduced to approximately 50 ml by means of an air stream. A slight excess of 10% sodium

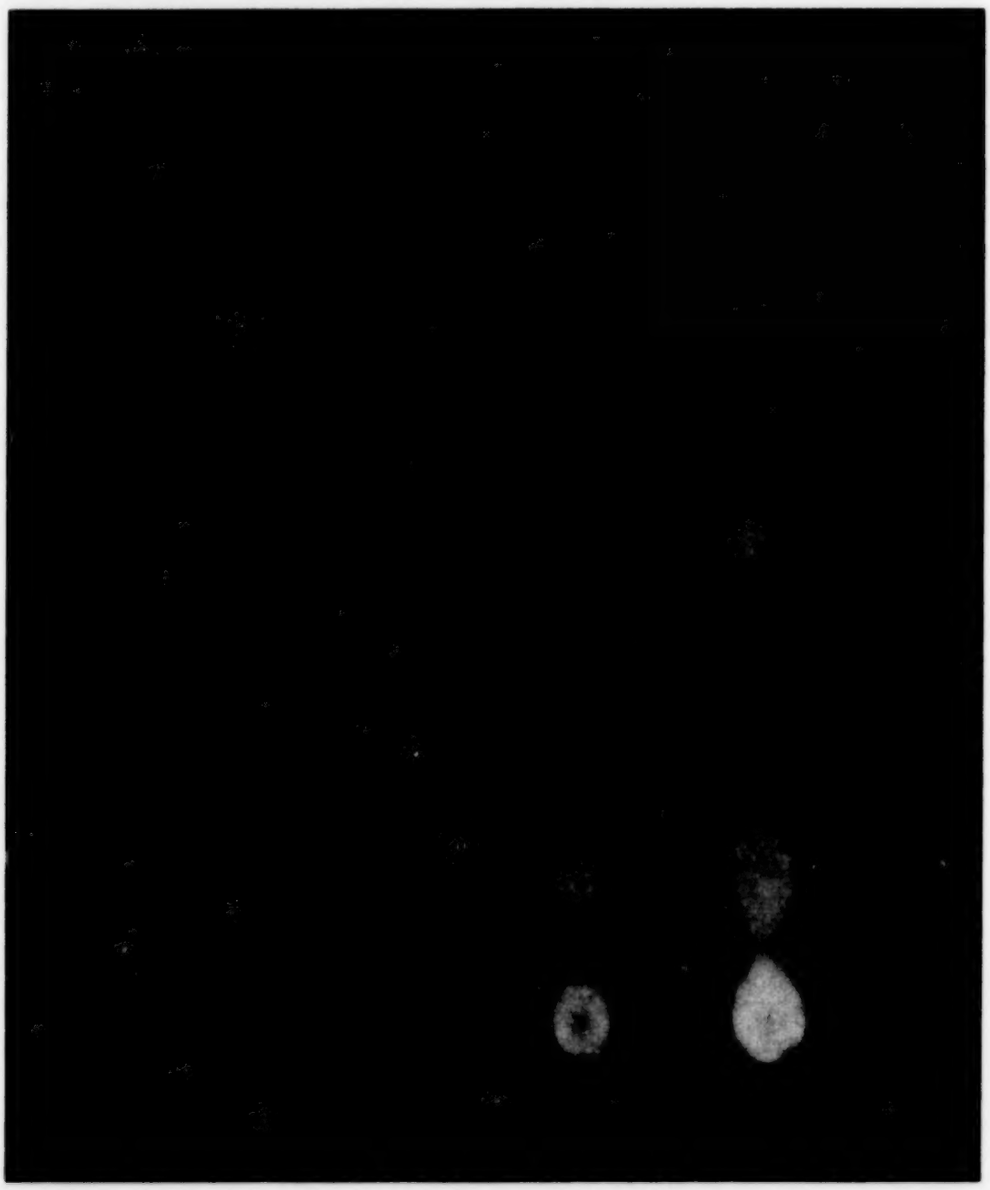

Fig. 2. Radioautograph of odd mixtures of straight chain N-benzamides.

hydroxide and 0.1 to 0.15 ml of radioactive benzoyl chloride were added, and the reaction mixture was shaken for 20 min. The benzamides were extracted with three portions of benzene, to make a total volume of approximately 40 ml. The benzene solution was evaporated in an air stream to a volume of 2–3 ml, diluted to 5 ml with additional benzene, and chromatographed as described above.

Atmospheric vapors were collected in approximately 10% sulfuric acid by means of a Smith-Greenburg impinger. The collected sample was neutralized with sodium hydroxide in a closed flask with a sidearm dipping into a container of ether. This trapped any vapor liberated during the neutralization. The aqueous layer was then extracted with ether, the ether layers were combined, and were treated as indicated above for the particulate matter.

RESULTS AND DISCUSSION

The data in Table I gives a survey of mean R_F values of the benzamides. These values are not to be taken as absolute, since they are influenced by some of the usual factors which cause variation in R_F values. The presence of foreign material as are found in air samples tend to depress the values still more.

Homologous benzamides are separated satisfactorily on Schleicher and Schüll 2040a gl. paper with a development time of 3 h, while isomeric benzamides, with the exception of the pair N-propyl and N-isopropyl, are not completely separated. Although the pair N-decyl and N-dodecyl benzamides are incompletely separated on S. & S. 2040a gl. paper in the standard development time, these are very satisfactorily separated on S. & S. 2045a gl. paper.

While secondary benzamides are separated from each other, they are not completely separated from some of the primary benzamides, so that spectra must be relied upon to differentiate them[9].

A typical separation of a mixture of N-ethyl, N-sec-butyl, N-hexyl, N-octyl, and

TABLE I

N-BENZAMIDES

R_F value × 100

N-Benzamide	*System M*	*System E*
S & S 2040a gl. paper		
N-methyl	3.60	4.49
N-ethyl	8.35	16.68
N-propyl	16.11	30.59
N-isopropyl	22.13	41.50
N-sec-butyl	33.75	58.29
N-isobutyl	29.63	61.87
N-*n*-butyl	33.90	
N-isoamyl	42.82	68.96
N-hexyl	62.62	82.28
N-heptyl	71.19	
N-octyl	81.82	
N-decyl	87.03	
N-dodecyl	89.30	
2-ethyl-N-hexyl	80.83	95.68
1,3-dimethyl-N-butyl	65.31	81.89
benzoic acid	16.0–19.43	44.18
N,N-diisopropyl	84.13	
N,N-diisobutyl	92.69	
S & S 2045a gl. paper		
N-decyl	75.37	
N-dodecyl	82.02	

TABLE II

N-BENZAMIDES FOUND IN AIR SAMPLES

Sample	*Benzamide found*	*mg Benzamide*	*Amine mg*	*Total air flow m³*	*Amine mg/m³ air*
Los Angeles	N-ethyl	3.045	0.920	1,800	$5.1 \cdot 10^{-5}$ [a]
Birmingham	None[b]	less than identifiable quantity		25,167	—
New York	N-methyl	3.516	0.808	5.44	0.149

[a] The air flow is estimated as an average of 2000 m³ per 24 h in the absence of specific air flow data.
[b] No individual benzamide could be identified.

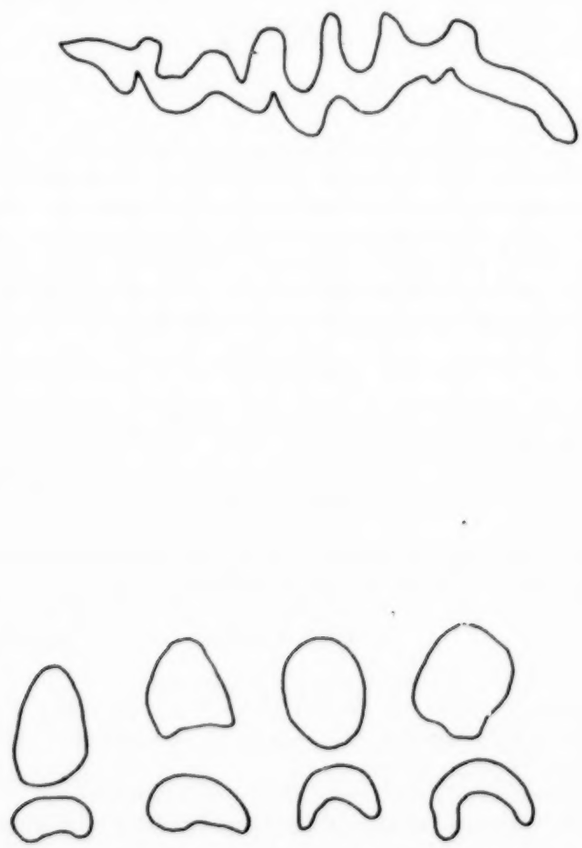

Fig. 3. Radioautograph of atmospheric vapors, New York City.

N-decyl benzamides is illustrated in Fig. 1, with the quantities increasing from 15 to 50 μg, while in Fig. 2 is illustrated a separation of N-methyl, N-propyl, N-isoamyl, and N-heptyl benzamides of the same magnitude.

A radioautograph of an air particulate sample from Los Angeles, California showed two distinct spots at R_F values corresponding to N-ethyl and possibly N-propyl benzamide plus benzoic acid. By rechromatographing these areas in system E they have been shown to be N-ethyl benzamide, and benzoic acid formed by the hydrolysis of benzoyl chloride. A larger area near the front of the chromatogram was produced by a yellowish material which gave a reddish fluorescence under ultraviolet light.

A similar radioautograph of air particulate matter from Birmingham, Ala., showed no such spots other than benzoic acid and the large frontal smear.

Fig. 3 is a representation of a chromatogram of a sample of atmospheric vapors collected in approximately 10% H_2SO_4 in a New York City fish market. Two distinct spots are visible at R_F values corresponding to N-methyl benzamide and the expected benzoic acid area. The approximate values of the benzamides found in both the Los Angeles and the New York sample can be seen in Table II. These have been estimated by a modification of the isotope dilution method[10] and by spectrophotometry.

ACKNOWLEDGEMENTS

The authors are indebted to DR. L. M. MARSHALL for suggesting the problem and for stimulating discussions on the subject. We are also grateful to DR. MORRIS B. JACOBS for furnishing us with the sample from New York City. The Los Angeles sample was collected by the National Air Sampling Network.

SUMMARY

A method is described for the separation of amines as their benzamides by paper chromatography. Data are given on separations in two systems. Homologous benzamides from C_1 to C_{10} are best separated on S & S 2040a paper while C_{10} and C_{12} are separated on 2045a paper. When radiocarbon labelled benzamides were chromatographed and placed on x-ray film for eight to ten days with subsequent development of the radioautograph, the lower limit of identification was found to be *ca.* 2.5 μg of each benzamide. The results of analysis for amines in two samples of air particulate matter, and one of atmospheric vapors are presented.

RÉSUMÉ

Une méthode chromatographique et radiochimique est décrite pour la séparation et l'identification des amines aliphatiques contenues dans l'air.

ZUSAMMENFASSUNG

Beschreibung einer papierchromatographischen und radiochemischen Methode zur Trennung und Bestimmung von aliphatischen Amine in der Atmosphäre.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM(II) WITH 5(*p*-DIMETHYLAMINOBENZYLIDENE)RHODANINE*

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In 1928 FEIGL[1] reported that rhodanine and many of its derivatives gave precipitates with silver ion and mercuric ion, and that 5(*p*-dimethylaminobenzylidene)rhodanine (hereinafter designated DMABR for brevity) was especially suitable as a sensitive, specific reagent for silver. In a study of spot test methods for the noble metals, HOLZER[2] reported that DMABR was a sensitive reagent for silver, gold, platinum, and palladium; depending upon the concentration of the metal in solution, the spot from palladium was bright red-violet to black-violet, and was reported to be readily distinguishable from the color produced by the other elements. FEIGL, KRUMHOLZ AND RAJMANN[3] used DMABR for the detection of silver, gold, and palladium; palladium salts gave a violet precipitate, and platinum and iridium also gave positive tests with the reagent, but not as readily. Osmium, rhodium, and ruthenium were reported to give no reaction. The limit of detection of palladium, in 0.1 *N* hydrochloric acid solution, was given as 0.66 μg in solution and 0.01 μg on spot test paper.

The purpose of the present investigation was to develop a spectrophotometric method for palladium using DMABR reagent, and to endeavor to determine the nature of the color reaction.

APPARATUS

Spectral curves were recorded with a Beckman Model DK-1 spectrophotometer. A Beckman Model DU spectrophotometer was used for making more precise absorbance measurements at a given wave length. Matched silica cells of 1.00-cm optical path were used. The instruments were located in a constant temperature room (26°) and no further attempt was made to control the temperature of the solutions measured.

Measurements of pH were made with a Beckman Model H-2 pH meter, using glass and calomel electrodes.

Calibrated weights and calibrated volumetric ware were used.

REAGENTS

Standard palladium solution

Exactly 0.5000 g of palladium metal powder (A. D. Mackay, Inc.) was dissolved

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in aqua regia. The solution was evaporated twice with hydrochloric acid to destroy nitric acid; the residual solution, having a volume of about 45 ml, was diluted with water to 500 ml (volumetric flask). This stock solution, 1000 p.p.m. in palladium and about 0.5 *N* in hydrochloric acid, was assayed by precipitation and weighing as palladium dimethylglyoximate[4]. The palladium found in triplicate 20.00-ml aliquots was 19.95, 19.94, and 19.95 mg. Working solutions were prepared as needed by volumetric dilution of the stock solution.

DMABR

The 5(*p*-dimethylaminobenzylidene)rhodanine (Eastman No. 2748) was used as received. Two different lots gave slight differences in absorbance and in wave length of absorption maximum of the developed palladium solution; recalibration is therefore indicated when a different lot of reagent is put into use. Preliminary tests showed that the reagent was more soluble and also more stable in formic acid than in ethanol, acetic acid, or hydrochloric acid. The reagent stock solution was prepared quantitatively by dissolving a known weight of the solid DMABR in 88% formic acid; working solutions were prepared by volumetric dilution. The stock solution was stable for at least 2 months.

Organic acids

Formic acid (88%) and glacial acetic acid (99.7%) were analytical reagent grade. Propionic acid was Eastman No. 396, b.p. 141–143°.

Other reagents

Substances used in interference tests were obtained as or prepared from reagent quality chemicals. Chlorides of iron(III), cobalt(II), nickel(II), chromium(III), copper(II), mercury(II), rhodium(III), iridium(III) and ruthenium(III) were used as sources of the respective metal ions, and potassium dichromate was used for chromium(VI). Solutions of gold(III) and platinum(IV) were prepared from the pure metals by dissolution in aqua regia and repeated evaporation with hydrochloric acid. Osmium tetroxide was dissolved in sodium hydroxide solution, which was then acidified with hydrochloric acid. Sodium or potassium salts were used as sources for the anions.

EXPERIMENTAL

Preliminary experiments

The red to violet precipitate formed in neutral or slightly acidic solution with DMABR in ethyl alcohol is a sensitive spot test for palladium[2]. The principal problem in using this reaction as a spectrophotometric method was to find a condition and/or solvent to prevent the formation of the precipitate. In solution buffered at pH 4, palladium (1–4 p.p.m.) and DMABR in ethyl alcohol gave a red-violet solution having an absorption maximum at 480 mμ. However, within a few minutes a red turbidity developed; similar precipitates were obtained at higher pH, up to pH 10. N,N-dimethylformamide was effective in preventing precipitation, but the absorption maximum varied from 480 to 515 mμ, depending upon the amount of solvent used, and absorbances were not well reproducible. In addition, the reagent blank in N,N-dimethylformamide (orange solution) showed extensive absorption in the same region as the

palladium product, and the reagent solution in N,N-dimethylformamide was stable for only a few days. Preparations in formic, hydrochloric, acetic, or propionic acid medium were more soluble and more stable, and these systems were investigated in detail.

Formic acid solutions

The influence of each different variable was evaluated singly by maintaining other factors constant. Solutions of the reactants were mixed to a final volume of 10.0 ml; after allowing 10 min for color development the absorbance was measured at the absorption maximum of 515 mμ.

Concentration of DMABR

3 ml of 0.10 *N* hydrochloric acid containing 10 μg of palladium was mixed with 1.0 ml to 5.0 ml of 0.01% DMABR in 44% formic acid and 6.0 to 2.0 ml of 44% formic acid. The absorbance increased only slightly with the amount of DMABR, reaching a maximum of 0.412 at 3.0 and 4.0 ml of the reagent solution.

Formic acid concentration

1 ml of solution containing 10 μg of palladium and 1.0 ml of 0.04% DMABR (in 44% formic acid) were mixed with 1.0 to 5.0 ml of 88% formic acid and 7.0 to 3.0 ml of water. Absorbance measurements were as follows:

ml of 88% formic acid:	1.0	2.0	3.0	4.0	5.0
ml of water:	7.0	6.0	5.0	4.0	3.0
absorbance at 515 mμ:	ppt.	0.423	0.438	0.183	0.015

Hydrochloric acid concentration

1 ml of solution containing 10 μg of palladium and 4.0 ml of 0.01% DMABR in 44% formic acid were mixed with 0.0 to 4.0 ml of 0.10 *N* hydrochloric acid and 5.0 to 1.0 ml of water. Absorbance measurements were as follows:

ml of 0.10 *N* HCl:	0	1.0	2.0	3.0	4.0
ml of water:	5.0	4.0	3.0	2.0	1.0
absorbance at 515 mμ:	0.435	0.415	0.405	0.388	0.322

Solutions containing 2.0 or 3.0 ml of 0.10 *N* hydrochloric acid attained maximum absorbance most rapidly, and were more stable against precipitation than solutions of lower or of higher acid concentration.

Procedure

Transfer 3.0 ml of 0.10 *N* hydrochloric acid containing 5 to 25 μg of palladium to a dry 10-ml volumetric flask; add 3.0 ml of 88% formic acid, 1.0 ml of DMABR reagent (0.04% solution in 44% formic acid); dilute to volume with water. Allow 7 to 10 min for color development, then measure the absorbance at 515 mμ against a reagent blank.

The system conforms to Beer's law, as shown by the data in Table I. The specific

absorptivity, 0.406 per p.p.m.–cm, corresponds to a palladium absorptivity of $4.32 \cdot 10^4$ l mole^{-1}cm^{-1}.

TABLE I

CALIBRATION DATA

Pd conc., p.p.m.	*In formic acid*		*In hydrochloric acid*		*In propionic acid*	
	Absorbance at 515 mμ	*Absorptivity, p.p.m.$^{-1}$ cm^{-1}*	*Absorbance at 515 mμ*	*Absorptivity p.p.m.$^{-1}$ cm^{-1}*	*Absorbance at 530 mμ*	*Absorptivity, p.p.m.$^{-1}$ cm^{-1}*
0.50	0.210	0.420	0.205	0.410	0.187	0.374
1.0	0.407	0.407	0.399	0.399	0.378	0.378
1.5	0.603	0.402	0.583	0.389	0.567	0.378
2.0	0.802	0.401	0.785	0.393	0.763	0.381
2.5	1.000	0.400	0.970	0.388	0.963	0.385
Average:		0.406		0.396		0.379
Average deviation:		0.006		0.007		0.003

Hydrochloric acid solutions

The same general procedure was used as with the formic acid solutions, for evaluating the influence of the variables. The absorption maximum occurred at 515 mμ.

Effect of hydrochloric acid concentration

1 ml of solution containing 10 μg of palladium was mixed with 3.0 ml of DMABR reagent solution, then was diluted to 10.0 ml with hydrochloric acid of different concentrations. Absorbance measurements were as follows:

HCl for dilution, *N*:	0.10	0.20	0.40	0.60	0.80
absorbance at 515 mμ:	0.400	0.370	0.327	0.200	0.033

At the two lowest acidities, maximum color development occurred almost immediately, and the absorbance was constant for about 45 min, after which it decreased slowly. At the higher acidities the initial absorbance decreased with increasing acid concentration, and the absorbance gradually increased with time, up to one hour (after which the measurements were discontinued).

Substitution of formic acid solution for part of the hydrochloric acid for dilution to volume decreased the absorbance, and increased the time required for full color development.

Procedure

Transfer 1.0 ml of solution containing 5 to 25 μg of palladium to a dry 10-ml volumetric flask; add 3.0 ml of DMABR reagent, and dilute to volume with 0.10 *N* hydrochloric acid. Measure the absorbance at 515 mμ against a reagent blank.

The data of Table I show that the system conforms to Beer's law; the average specific absorptivity is 0.396 per p.p.m.–cm. Solutions containing 0.50 p.p.m. of palladium were stable for about 45 min; the stability decreased with increasing palladium concentration, so that at 3.0 p.p.m. the absorbance was constant for less than 10 min. Eventually a dark red precipitate separated from all samples. The precision was tested by 10 preparations containing 1.0 p.p.m. of palladium in the final solution; the average absorbance was 0.399 ± 0.007.

Acetic acid solutions

When glacial acetic acid was used as the diluent, the absorption maximum occurred at 530 mμ. Although the system conformed to Beer's law and the reproducibility was satisfactory, the sensitivity for palladium was much lower than in other media; the specific absorptivity was only 0.052 per p.p.m.–cm. Samples required about 30 min for full color development, and the solutions were stable for about one hour.

Propionic acid solutions

Procedure

This procedure was adopted after a preliminary study of the variables. To a dry 10-ml volumetric flask transfer 2.0 ml of 0.05 *N* hydrochloric acid containing 5 to 25 μg of palladium. Add 1.0 ml of DMABR reagent (0.04% solution in 88% formic acid) and mix thoroughly. (A red-violet precipitate forms immediately; it is readily soluble in propionic acid). Dilute almost to volume with propionic acid and mix thoroughly; temperature and volume decrease on mixing. Bring the mixture to room temperature, and complete the dilution to volume with propionic acid. Prepare a corresponding blank. Allow 15 min for full color development and measure the absorbance at 530 mμ, the absorption maximum.

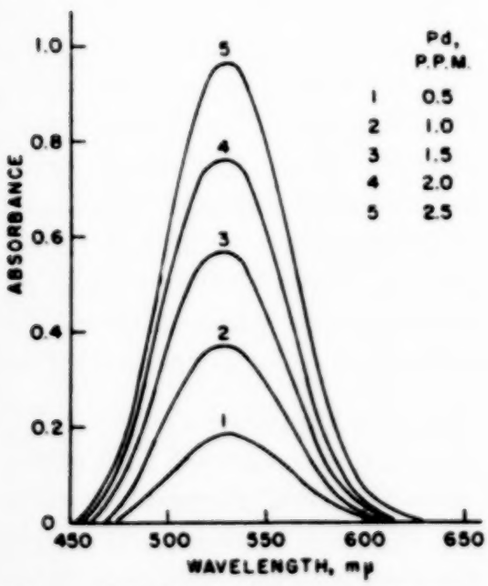


Fig. 1. Palladium–DMABR system in propionic acid solution.

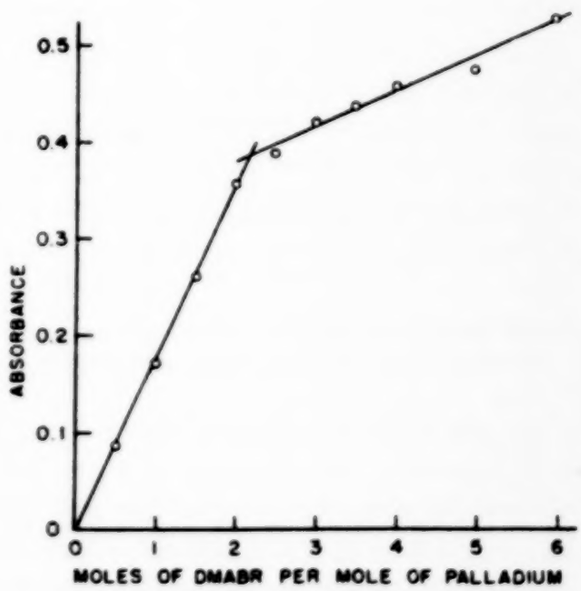


Fig. 2. Mole ratio plot for palladium–DMABR system.

The absorption spectra for several concentrations of palladium are shown in Fig. 1. The system conforms to Beer's law, as shown by data in Table I. The specific absorptivity of 0.379 per p.p.m.–cm corresponds to a palladium absorptivity of $4.03 \cdot 10^4$ l mole^{-1} cm^{-1}.

Stability

The solutions showed constant absorbance for at least two hours, then faded slowly over a period of 24 h (measurements were not continued beyond this time). No precipitate appeared even after several days.

Effect of foreign ions

Solutions containing 1.0 p.p.m. of palladium and varying amounts of diverse ions were color-developed and measured by the standard procedure. The tolerance for a foreign ion was taken as the largest amount of the ion that could be present with the palladium and give a transmittance within 0.4% (absolute) of that of the palladium alone; at the 1.0 p.p.m. palladium level a difference of 0.4% transmittance corresponds to an absorbance difference of about 0.005. Interference tests were made in both the hydrochloric acid and the propionic acid solution. The results are summarized in Table II.

TABLE II

EFFECT OF FOREIGN IONS

Palladium concentration, 1.0 p.p.m.

Foreign ion	*Tolerance, in p.p.m.*	
	Hydrochloric acid solution	*Propionic acid solution*
Platinum(IV)	200	20[a]
Rhodium(III)	10	300
Iridium(III)	20	10
Ruthenium(III)	10	20
Osmium(IV)	100	100
Gold(III)	0	0
Iron(III)	50	10
Cobalt(II)	200	300
Nickel(II)	100	300
Chromium(III)	300	
Chromium(VI)		2
Copper(II)		5
Mercury(II)		100
Nitrate		>200
Sulfate		>300

[a] This tolerance applies only if absorbance is measured within 15 min; platinum(IV) slowly develops a red solution which absorbs strongly at 525–530 mμ.

By the method reported here for palladium, silver ion is precipitated as silver chloride; however, the amount of silver ion remaining in solution saturated with silver chloride is sufficient to give the characteristic color with DMABR. Preliminary tests have shown that the violet color formed by reaction of DMABR with gold(III) could be used as a spectrophotometric method for the latter in the concentration range of a few p.p.m.

COMPOSITION OF THE REACTION PRODUCT

The stoichiometry of the palladium–DMABR reaction was investigated spectrophotometrically by the mole ratio method[5], the method of continuous variations[6], and the slope ratio method[7]. The precipitate formed by the reaction was also subjected to elemental analysis.

Mole ratio method

A series of solutions was prepared from a constant amount of palladium ($1.0 \cdot 10^{-7}$ mole) and varied amounts of DMABR ($0.5–7.0 \cdot 10^{-7}$ mole). 3 ml of palladium solution (in 0.1 *N* hydrochloric acid) and 3 ml of DMABR solution were diluted to 10.0 ml

with 0.10 *N* hydrochloric acid. Absorbances were measured at several wave lengths around the absorbance maximum. Plots of absorbance (at a given wave length) against the mole ratio of DMABR to palladium showed a distinct change of slope at a 2 : 1 ratio. Solutions of the DMABR reagent in formic–hydrochloric acid show a considerable absorbance in the same region as the absorbance maximum of the DMABR–palladium product. The absorbances of DMABR solutions of various concentrations were measured against a formic–hydrochloric acid blank. The data for the DMABR–palladium solutions were corrected for the absorbance due to unreacted DMABR in excess of the 2 : 1 ratio to palladium; the break in the absorbance *vs.* mole ratio plot was thereby sharpened. The plot was also linear, after the break at the 2 : 1 mole ratio, up to at least a 7 : 1 mole ratio, indicating the 2 : 1 product as the only (absorbing) reaction product formed.

The experiments were repeated with solutions diluted with propionic acid instead of with hydrochloric acid. The absorbance *vs.* mole ratio plots again showed sharp breaks at a 2 : 1 mole ratio of DMABR to palladium. A typical plot is shown in Fig. 2.

Continuous variations method

The palladium solution was $2.0 \cdot 10^{-4}$ *M*, in 0.10 *N* hydrochloric acid; the DMABR, also $2.0 \cdot 10^{-4}$ *M*, was in 88% formic acid solution. The solutions were mixed in the ratio of *x* ml of DMABR to 5.0 — *x* ml of palladium, and were then diluted to 50 ml with 88% formic acid and 0.10 *N* hydrochloric acid in such proportion that these acids would be present in the same amounts in all samples. Absorbance was measured at several wave lengths around the absorbance maximum. The absorbance data were corrected for any excess DMABR or excess palladium, assuming a 2 : 1 reaction ratio as indicated by the mole ratio study. A plot of absorbance against mole fraction of DMABR showed a sharp maximum at a mole fraction of 0.67, representing a 2 : 1 mole ratio of DMABR to palladium in the color reaction.

The same results were obtained with solutions in which the reactants were diluted with propionic acid. A typical continuous variations plot is shown in Fig. 3.

Slope ratio method

In one series of solutions the amount of DMABR was kept constant ($6.0 \cdot 10^{-7}$ mole) and large with respect to the varying amounts of palladium ($0.5–2.0 \cdot 10^{-7}$ mole). In the second series the amount of palladium was kept constant and equal to the concentration of the DMABR in the first series, and the amount of DMABR reagent was varied from $0.5–2.0 \cdot 10^{-7}$ mole. The reactants were diluted to volume with propionic acid. The plot of absorbance against concentration of the variable component is shown in Fig. 4; the right-hand ordinate scale has been displaced downward by the amount of the absorbance of the DMABR solution alone; in this way the origins of the two curves coincide, and the ratio of their slopes is more readily apparent. The ratio of the slopes of the two curves is very nearly 2 : 1, again confirming the 2 : 1 reaction ratio of DMABR to palladium.

Elemental analysis

Palladium(II) solution (200 mg in 200 ml) was precipitated by dropwise addition of 1% DMABR solution (in formic acid). After standing overnight the precipitate

was further settled by centrifugation. The supernatant solution was removed and the precipitate was washed repeatedly with 95% alcohol, after which it was dried in a vacuum desiccator over anhydrous magnesium perchlorate. Flaky, red-violet crystals were obtained. (Attempts to recrystallize the product from formic acid resulted in an apparently amorphous mass). Different preparations were submitted to each of two different analytical laboratories for elemental analysis. The results for carbon, hydrogen, nitrogen, and sulfur were in such poor agreement as to be of no value in trying to deduce the stoichiometric composition of the precipitate. Obviously, the precipitate was not pure, probably as a result of absorption and/or solvation in the preparation, and no further attempt was made along this line.

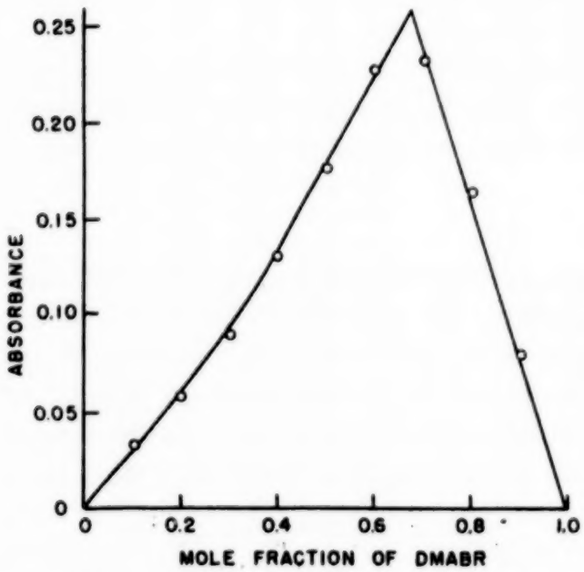


Fig. 3. Continuous variations plot for palladium–DMABR system.

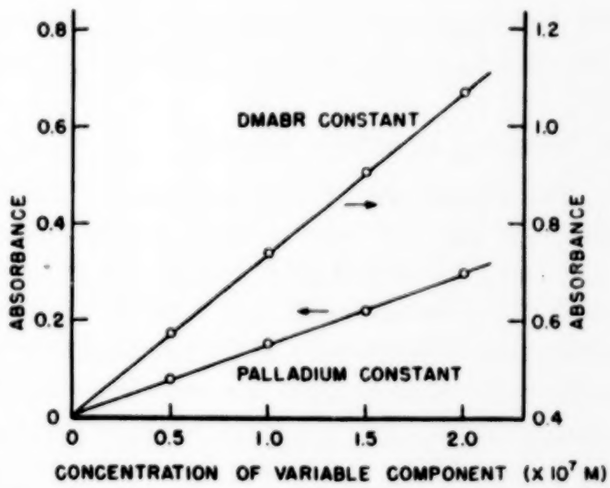
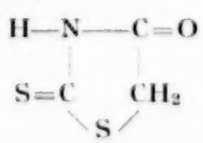


Fig. 4. Slope ratio plot for palladium–DMABR system.

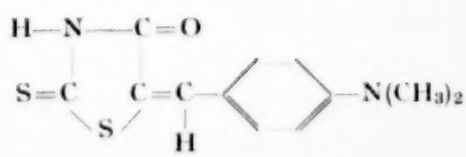
DISCUSSION

The method reported here compares favorably in sensitivity with other spectrophotometric methods for palladium; a summary of several methods has been given by AYRES AND ALSOP[4].

The reaction of rhodanine (I) and its derivatives, including 5(*p*-dimethylaminobenzylidene)rhodanine (II),



I. Rhodanine



II. 5(*p*-dimethylaminobenzylidene)-rhodanine (DMABR)

with various metal ions has been studied extensively[2,3,8–11]. Deductions from these studies lead to the conclusion that the $=N-\underset{\underset{S}{\|}}{C}-S-$ group is probably responsible for reactions with metal ions. The nitrogen and sulfur atoms in this group are capable of acting as electron-pair donors. If DMABR acts as a bidentate coordinator and in a 2 : 1 mole ratio with palladium, as was found experimentally by the spectrophoto-

metric methods, a complex ion of the empirical formula $[Pd(DMABR)_2]^{+2}$ might be formed. Three different structures would be possible, depending upon which of the atoms of the $=N-\underset{\underset{S}{\|}}{C}-S-$ group served as electron-pair donors, but each of these possible structures would involve a 4-membered ring having considerable strain. It seems likely, also, that there would be steric effects operating against the formation of such structures. If the reactants form a complex ion as postulated above, the precipitate formed might be represented by $Pd(DMABR)_2X_2$, in which X represents a univalent anion such as chloride, formate, or propionate. Test for chloride, after sodium fusion of the precipitate, was negative, as was also a test for formate and propionate with chromotropic acid, after dissolution of the precipitate in sulfuric acid.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial assistance provided by National Science Foundation grant NSF G1889 and by The University of Texas Research Institute project 637.

SUMMARY

A sensitive spectrophotometric method has been developed for the determination of palladium, using 5(*p*-dimethylaminobenzylidene)rhodanine reagent in formic, hydrochloric, or propionic acid solution. The systems conform to Beer's law. The specific absorptivity is in the range 0.38 to 0.40 per p.p.m.–cm in the different solvents. The optimum range for 1.00-cm optical path is about 0.4 to 2.5 p.p.m. of palladium. At higher concentrations of palladium a violet-red precipitate forms within a few minutes. In propionic acid solution maximum color is attained at room temperature in 10 to 15 min, and is stable for more than two hours. The system is somewhat sensitive to hydrogen ion concentration; maximum absorbance and stability are attained at 0.01 *N* hydrochloric acid in the final solution. Platinum(IV), ruthenium(III), iridium(III), iron(III), chromium(VI), and copper(II) interfere if present in amounts several times greater than the amount of palladium; gold(III) interferes very extensively. The mole ratio method, the continuous variations method, and the slope ratio method all show the mole ratio of DMABR to palladium to be 2 : 1 in the color-forming reaction.

RÉSUMÉ

Une méthode spectrophotométrique sensible est proposée pour le dosage du palladium, au moyen de *p*-diméthylaminobenzylidènerhodanine. Le dosage s'effectue en milieu formique, chlorhydrique ou propionique. Il convient pour des teneurs en palladium de 0.4 à 2.5 p.p.m.; à des concentrations plus élevées, il y a formation d'un précipité violet.

ZUSAMMENFASSUNG

Beschreibung einer empfindlichen spektrophotometrischen Methode zur Bestimmung von Palladium mit Hilfe von *p*-Dimethylaminobenzylidenrhodanin in salzsaurer-, ameisensaurer oder propionsaurer Lösung. Der geeignete Konzentrationsbereich liegt zwischen 0.4 und 2.5 p.p.m.; bei höheren Konzentrationen an Palladium entsteht nach wenigen Minuten ein rotvioletter Niederschlag.

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IDENTIFICATION OF PHOSPHATE ANIONS IN NIOBIUM AND TANTALUM PHOSPHATES BY MEANS OF INFRA-RED SPECTRA

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The infra-red absorption spectra of many inorganic compounds have been studied recently, and methods have been devised for the identification and even the determination of many substances. Compilations of infra-red spectra have been published by MILLER AND WILKINS[1] and by HUNT *et al.*[2,3]. MILLER AND WILKINS recorded the spectra of a few orthophosphates but the most important contribution to infra-red studies of solid metal phosphates was made by CORBRIDGE AND LOWE[4]. Many of the observed bands in the infra-red region prove to be due to phosphate anions and arise from stretching vibrations in phosphorus–oxygen bonds. These bands are, as expected, quite different in solids containing orthophosphate, pyrophosphate, and polyphosphate anions, and infra-red examination apparently provides a direct experimental means of identifying the type of anion present in a solid phosphate. With the standard information of CORBRIDGE AND LOWE[4] as a basis, infra-red examination of some niobium and tantalum phosphates and also zirconium pyrophosphate was undertaken in the hope of establishing the types of phosphate anion present in them.

EXPERIMENTAL

Apparatus and techniques

The absorption spectra were recorded on a Perkin-Elmer Model 21, double beam instrument in which a rock-salt prism was used. All spectra were recorded over the wave-number range 600–4000 cm^{-1}. The conventional method of "mulling" the finely powdered specimens in "Nujol", developed by KELLER AND PICKETT[5], was employed, since the absorption bands of "Nujol" did not interfere with the characteristic phosphate bands in the region 650–1350 cm^{-1}. Sodium chloride disks were used to contain the mulls.

Reference substances

Magnesium pyrophosphate was prepared by igniting magnesium ammonium phosphate. Disodium hydrogen phosphate was the commercially available material of "AnalaR" grade; this was also used to prepare sodium orthophosphate by the method of HALL[6], and to prepare sodium triphosphate by the method of AUDRIETH[7].

Infra-red spectra of these reference substances were found to be in good agreement with those recorded by CORBRIDGE AND LOWE[4].

Results

Infra-red spectra of niobium phosphate ($Nb_2O_5 \cdot 2\ P_2O_5$), magnesium pyrophosphate ($Mg_2P_2O_7$) and zirconium pyrophosphate (ZrP_2O_7) are shown in Fig. 1. The absorption peaks are listed in Table I, the wave number being given in cm^{-1}.

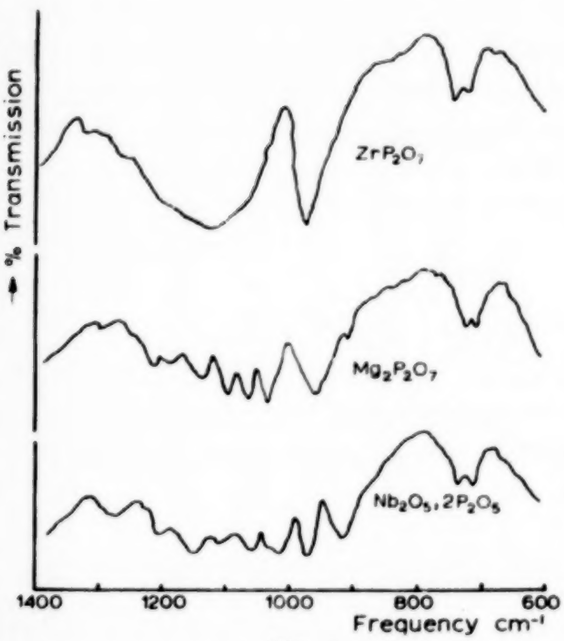

Fig. 1.

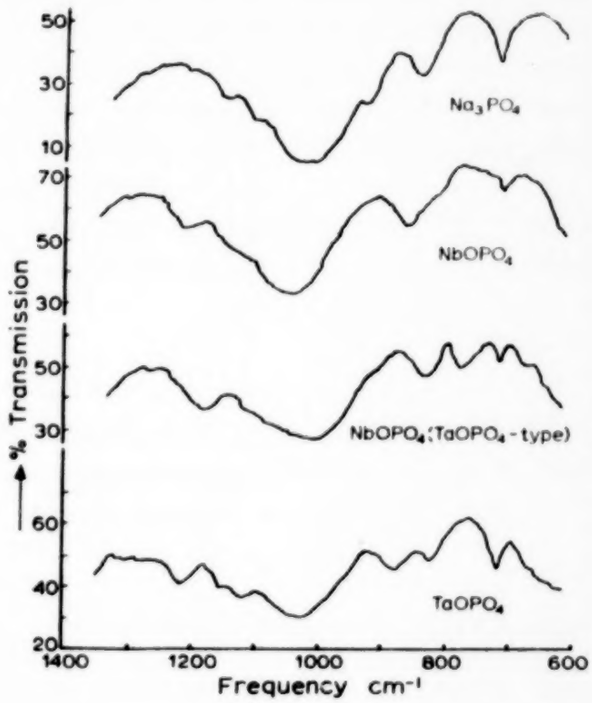

Fig. 2.

TABLE I

$Nb_2O_5 \cdot 2\ P_2O_5$		*ZrP_2O_7*		*$Mg_2P_2O_7$ (found)*		*$Mg_2P_2O_7$ (Corbridge and Lowe)*	
715	s	720	s	710	s		
730	w	740	w	725	w	725	m
915	vs	975	vs	910	w	907	m
975	s	1075 to 1125	sb	970	sb	932	m
1015	m			1045	m	1008	w
1055	w			1065	m	1049	m
1125	w			1100	w		
		1155	w				
1155	m			1130	m	1122	vs
1210	w			1205	m	1161	vs

vs = very strong, s = strong, m = medium, w = weak and b = broad

TABLE II

$NbOPO_4$		*$TaOPO_4$*		*$NbOPO_4$ ($TaOPO_4$ structure type)*		*Na_3PO_4 (found)*		*Na_3PO_4 (Corbridge and Lowe)*	
860	mb	825	m	772	m	845	sb	914	ww
1025 to 1065	vsb	860	mb	830	s	930	w		
		1010 to 1060	vsb	990 to 1050	vsb	985 to 1070	vsb	1028 to 1125	vsb sb
1150	w								
1210	w	1110	w						
		1210	m	1175	m	1150	w		

Infra-red spectra of $NbOPO_4$, $TaOPO_4$, $NbOPO_4$ (structure type $TaOPO_4$) and Na_3PO_4 are reproduced in Fig. 2. The absorption bands are listed in Table II.

The infra-red specimen of $Ta_2O_5 \cdot 3P_2O_5$ (TaP_3O_{10}) is compared with that of $Na_5P_3O_{10}$ (phase II) in Fig. 3. Absorption peaks are given in Table III.

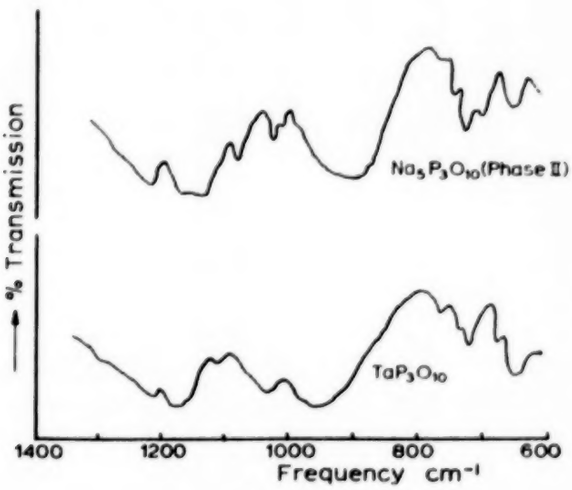

Fig. 3.

TABLE III

TaP_3O_{10}		$Na_5P_3O_{10}$ (phase II) (found)		$Na_5P_3O_{10}$ (phase II) (Corbridge and Lowe)	
655	m	655	m	665	s
725	s	715	w	737	m
760	w	730	m	906	vsb
930 to 975	vsb	745	w		
		890	sb	1016	w
1040	w	1010 to 1025	w	1098	s
1110	ww			1145	vs
1060 to 1175	vsb	1095	m	1165	s
1210	w	1145 to 1165	vsb	1184	s
		1215	m	1214	s

DISCUSSION

It was pointed out by CORBRIDGE AND LOWE[4] that the spectra of solid samples are liable to be influenced by a number of factors which are less important in pure liquids and liquid solutions. Absorption bands due to particular groups can be broadened, split, or shifted by interaction with other units in the structure (adjacent ions, water molecules, etc.) or by hydrogen bonding.

If the spectra of $Nb_2O_5 \cdot 2P_2O_5$, ZrP_2O_7 and $Mg_2P_2O_7$ are compared (Fig. 1), it is evident that whereas ZrP_2O_7 gives a simple spectrum the spectra of $Nb_2O_5 \cdot 2P_2O_5$ and $Mg_2P_2O_7$ are characterised by a large number of splittings; slight shifting of the

bands is apparent also. The general pattern, however, remains the same, and the presence of $P_2O_7^{-4}$ groups in all three structures appears likely.

In Fig. 2, the niobium and tantalum phosphates show very little splitting, but the broad band is somewhat displaced from the position in which it occurs in Na_3PO_4. The spectrum of tetragonal $NbOPO_4$ resembles more closely that of Na_3PO_4, whereas the spectra of $TaOPO_4$ and isomorphous $NbOPO_4$ are again similar. All these compounds show the general absorption pattern characteristic of PO_4^{-3} groups. It appears, therefore, that these substances are correctly regarded as orthophosphates. Polymerised phosphate anions in the niobium and tantalum salts would introduce absorption differences much greater than those indicated in Fig. 2.

The compound $Ta_2O_5 \cdot 3\ P_2O_5$ appears to be a true triphosphate, since it gives a spectrum (Fig. 3) closely related to that of sodium triphosphate (phase II) containing $P_3O_{10}^{-5}$ groups.

ACKNOWLEDGEMENTS

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SUMMARY

Some niobium and tantalum phosphates have been prepared and their infra-red spectra have been recorded and compared with those of reference substances. It has been possible to identify PO_4^{-3}, $P_2O_7^{-4}$ and possibly $P_3O_{10}^{-5}$ groups in different samples of niobium and tantalum phosphates.

RÉSUMÉ

Quelques phosphates de niobium et de tantale ont été préparés. Les spectres infra-rouge obtenus avec ces composés ont permis d'identifier les groupements PO_4^{-3}, $P_2O_7^{-4}$ et $P_3O_{10}^{-5}$.

ZUSAMMENFASSUNG

Es wurden die Infrarot Spektren einer Anzahl von Niob- und Tantalphosphaten aufgenommen und mit denen von Magnesium- und Natriumphosphaten verglichen, wobei PO_4^{-3}, $P_2O_7^{-4}$ und wahrscheinlich $P_3O_{10}^{-5}$ Gruppen nachgewiesen werden konnten.

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MECHANISM OF ELEMENTAL SPECTRAL EXCITATION IN FLAME PHOTOMETRY

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INTRODUCTION

In the course of studying flame photometry in high temperature flames (oxy–cyanogen, 5000°) and low temperature flames (oxy–hydrogen, 3000°), several interesting observations were made which are not explained by current interpretation of flame spectra. These were as follows:

(*1*) The flame acts as a U.V. source. The intensity of metal spectra increases with increased U.V. radiation from the flame, even when the temperature of the flame decreases.

(*2*) In oxy–hydrogen flames, metal spectral lines with wavelengths significantly less than 2800 Å are not usually observed.

(*3*) Organic solvents increase the spectral intensity many-fold.

Current theory leads us to believe that flame temperature is the main variable in controlling spectral intensity. Although it explains qualitatively the third of these observations, it does not explain the first two. In an effort to understand these phenomena, the following postulations were made: (*1*) Metal atoms are excited by ultraviolet light in the flame. (*2*) The metal must attain the excited atomic state before spectral emission can take place. (*3*) Some emitted energy is absorbed by the flame. (*4*) The mechanism of attaining the excited species is dependent on the solvent used[1].

WAVE MECHANICS

It has been shown elsewhere[1] that the intensity of a spectral line is governed by the equations

$$S = \frac{N_2 E}{\tau} = \frac{N_1 E}{\tau} \frac{g_1}{g_2} e^{-E/kT} \qquad (1)$$

and

$$\log Q = \frac{-5040\ V}{T} \qquad (2)$$

where S = Strengh of spectral line for the transition from excited to lower energy state
N_2 = No. of atoms in excited state
N_1 = No. of atoms in lower energy state
Q = $(N_2/N_1) \cdot (g_2/g_1)$
E = Energy difference between excited and lower energy state

V = E expressed in electron volts
g_1/g_2 = Statistical weights or a priori probabilities
k = Boltzman's constant
T = Temperature
τ = Life time of excited atoms

Eqn. (1) shows very clearly the relation between the temperature, T, of a system and the intensity of spectra, S, emitted from that system. It also shows that there is a relationship between the intensity S and the energy E associated with the particular spectral line being examined. Since

$$E = h\nu \tag{3}$$

where h = Planks constant
ν = Wave number = $1/\lambda$
λ = Wavelength of emitted spectral line

it follows that S is a function of λ for a given temperature. Providing the ratio g_1/g_2 does not vary significantly, and if N_2 is small compared to N_1 we would expect a relationship between the observed S and λ, and hence N_2/N_1 and λ to be as shown in Fig. 1.

Fig. 1 shows the mathematical ratio of excited atoms to unexcited atoms. It is very dependent on the energy difference, E, between N_2 and N_1 and hence λ for a constant temperature. It indicates that at this temperature (3000°K) we would expect to find, in general, that emission lines with wavelength 6000 Å would be 10^7 times as intense as emission lines at 2000 Å. At higher temperatures, of course, this difference would decrease, but would still remain orders of magnitude higher.

An examination of the M.I.T. tables of intensities of spectral lines[2] shows that although there is some tendency for this relationship to be true, the intensities are much nearer to being equal than would be indicated by the mathematical relationship. This is illustrated in Table I. The lines chosen were the strongest in their wavelength range.

We would expect from eqns. (1), (2) and (3) that under standardized conditions there would be a general tendency for intensity of emission lines to increase rapidly with increase in wavelength. However, Table I illustrates that this relationship does

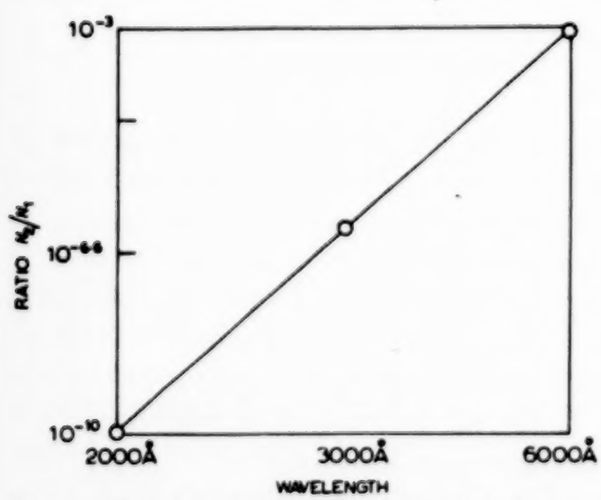

Fig. 1. Relation between N_2/N_1 and λ at a temperature of 3000°K.

TABLE I

Element	*λ Å*	*Intensity*
Sodium	5890	9000
	3302	600
Zinc	3075	150
	2138	800
Lead	4057	2000
Aluminium	3944	2000
	3082	800

not hold between the elements; neither does it hold for different spectral lines of the same element. For example, the sodium 5890 Å line should be about 10^4 as strong as the sodium 3032 Å line. Similarly, with zinc 3075 Å and 2138 Å lines. This leads to the conclusion that although the relationships shown in eqns. (1) and (2) are true in themselves, they do not tell the whole story.

It will be remembered that these equations were developed for studies of light emitted from stars where temperatures in the order of $5 \cdot 10^6$°K are encountered. Further, they were developed for black body conditions. At these temperatures of operation it is very probable that any other source of energy would be relatively unimportant. However, under laboratory conditions operating temperatures are much lower. Also, under laboratory conditions other sources of energy may play an important part. Ambient ultraviolet light is such an energy source. It happens that most sources for spectral excitation are also sources of U.V. light, *e.g.*, spectrographic arc and spark, flame photometers, etc.

The relationship between absorption and wavelength is given by the equation

$$I = I_0 e^{-K_\nu C l}$$

$$\int K_\nu d\nu = \frac{\pi e^2}{mc} N_\nu f$$

where I_0 = Intensity of transmitted light
I_1 = Intensity of transmitted light after absorption
K_ν = Absorption coefficient at wavenumber ν
C = Concentration
l = Path length
N_ν = Number of atoms which can absorb at wavenumber ν
f = Oscillator strength
m = Mass of the electron
c = Speed of light

As can be seen, the controlling variables are N_ν and f. The present work has been restricted to flame sources, but the conclusions should apply to spectrographic emission.

EXPERIMENTAL

It was considered that a flame offered advantages over other sources because its temperature and the spectral character could be varied independently. This allowed a study to be made of the effect of U.V. light at constant temperatures.

The flame as a source of ultraviolet light

Two types of flames were studied: (*a*) oxy–hydrogen, and (*b*) oxy–cyanogen. It was found by scanning the U.V. emission spectra of these flames that the intensity of emission could be changed considerably by changing the ratio of fuel to oxygen. It was further observed that the intensity of emission of iron spectral lines excited by these flames increased with increased U.V. light in the flame although the flame was below the maximum temperature in these cases. The results are summarized in Table II.

Results indicated increased metal emission with increased U.V. intensity in the flame but not with increased temperature. It should be noted that increased U.V. emission occurred with excess oxygen in the hydrogen flame and excess cyanogen in the second case.

Further evidence for this postulation was obtained when it was observed with the

TABLE II

RELATION BETWEEN INTENSITY OF EMISSION AND FLAME TEMPERATURE AND U.V. INTENSITY

	Oxy–Hydrogen			*Oxy–Cyanogen*		
	Excess H_2	*Stoichiometric (hottest)*	*Excess O_2*	*Excess $(CN)_2$*	*Stoichiometric (hottest)*	*Excess O_2*
Temperature	low	medium	low	medium	high	medium
U.V. emission (3060 Å water band)	medium	medium	high	high	low	low
Fe emission (3440 Å doublet)	medium	medium	high	high	low	low

oxy–hydrogen flame that spectral lines with wavelengths significantly below 3000 Å were not usually detected although many metals have intense spectrographic lines in this region, *e.g.*, lead 2393 Å, platinum 2165 Å, 2830 Å. It was noted that intense flame emission occurred at 3060 Å (OH-bands) and that metal emission lines with longer wavelengths were usually observed.

If it is conceded that the metals are excited by U.V. light, it is logical that the intense flame radiation at 3060 Å is the shortest wavelength excitation source. Wave mechanics tells us that this radiation may excite lines of longer wavelength, but not shorter wavelength. This fits in closely with experimental observation.

The results obtained with oxy–hydrogen flames are illustrated in Fig. 2. They show that using a mol ratio 1:1 of oxygen and hydrogen, the OH-bands are more intense although the flame temperature is lower and the temperature of the stoichiometric 1:2 ratio (O_2:H_2) flame. This increase in sensitivity of OH-bands coincided with an increase in intensity of the iron lines emitted when an iron solution is aspirated into these flames.

More supporting evidence was found when a similar study was made using an

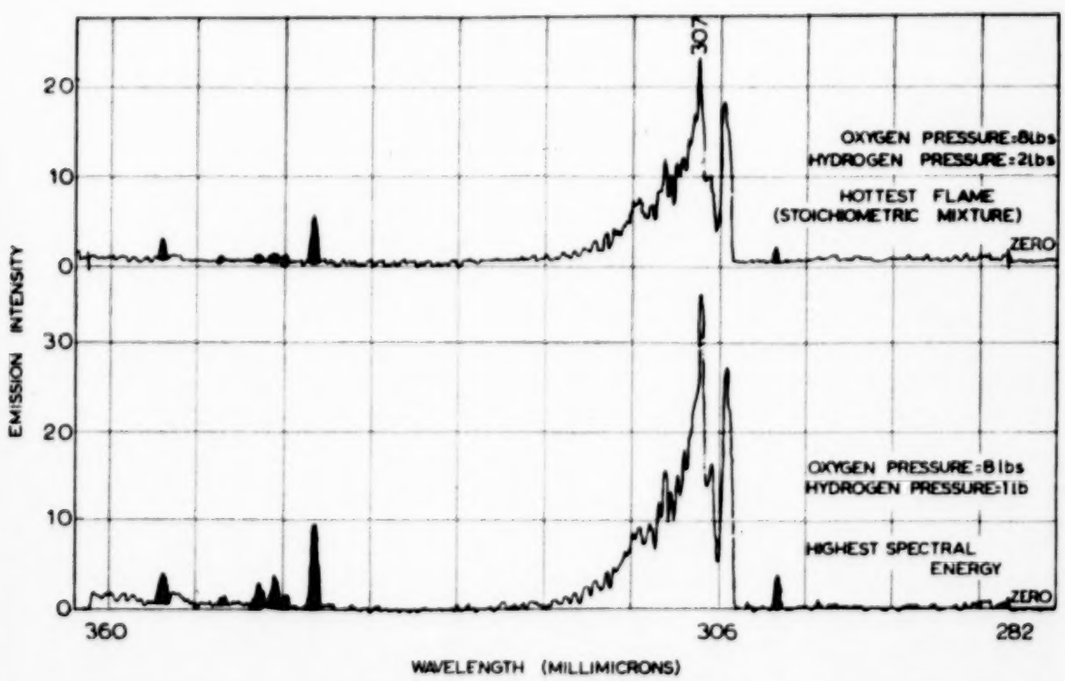

Fig. 2. Spectra of iron in oxy–hydrogen flames Iron lines (blacked in) superimposed on oxy–hydrogen flame spectrum.

oxy–cyanogen flame. The results are shown in Fig. 3. This shows the spectra between 2300 Å and 3000 Å exhibited by oxy–cyanogen flames set at the same temperature. In one flame there was excess oxygen. Very little, if any, U.V. radiation was detected. When iron was atomized into this flame, no spectral lines were observed in this region. The second flame contained excess cyanogen. Since these two flames were at equal temperatures, spectral variation could not be caused by temperature differences. However, this flame exhibited strong U.V. emission in the range 2300–3000 Å. When iron was atomized into this flame, numerous spectral lines were exhibited as can be seen.

These two flames differ only in their spectral character, their temperatures being equal. It seems likely, therefore, that the difference in excitation of iron spectrum is caused by the difference in U.V. light in the flame.

To summarize, if temperature were the only source of excitation, then all spectral lines, even down to 2000 Å would be excited in a flame. However, we have seen that normally only lines with wavelengths greater than 2800 Å are excited. This coincides with the wavelength of the intense lines found in oxy–hydrogen and oxy–cyanogen flames. Further, when the oxy–cyanogen flame is distorted to radiate short wavelength U.V. light, then metal emission lines are detected throughout the wavelength band 2000 Å to 3000 Å.

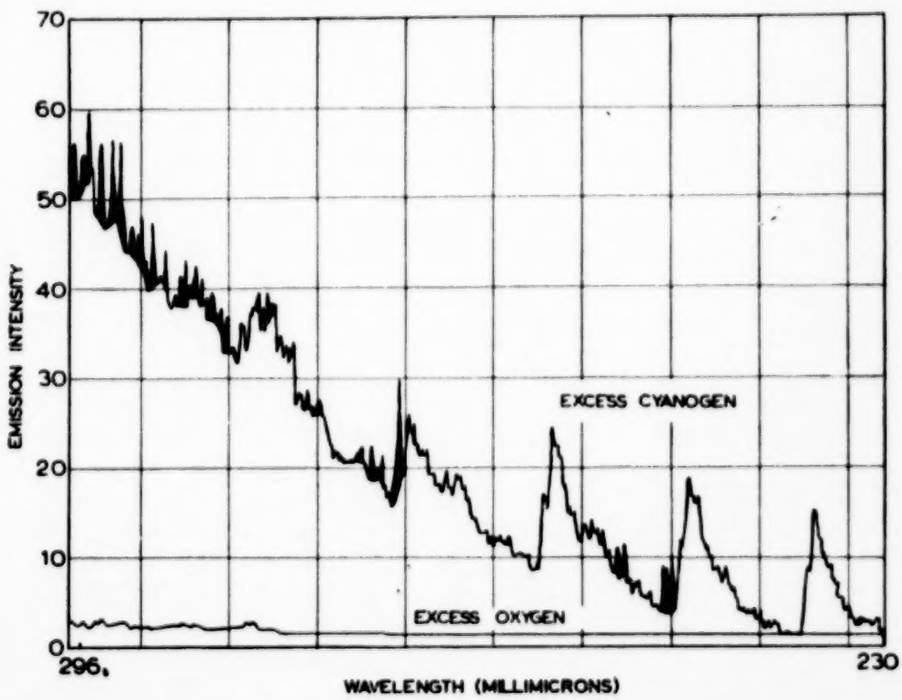

Fig. 3. Spectrum of iron in oxy–cyanogen flame. Iron lines (blacked in) superimposed on oxy–cyanogen flame spectrum. Note: Cyanogen flame with excess oxygen generates no U.V. light or iron spectrum although the temperature of both flames was equal.

Measurement of flame temperature

The most widely used method of measuring flame temperatures are the line reversal technique[3], and vibrational band intensity technique. However, these procedures are accurate to about $\pm 20°$. Further, it requires experience and skill to obtain reliable results and, of course, difficulty would be expected in calibrating at 5000°, a temperature range not normally used. It was decided, therefore, to use an alternate technique. A diagram of the equipment is shown in Fig. 4.

The thermistor was sensitive to very small changes in temperature. Also, it has a small heat capacity, ensuring a short response time to come to equilibrium. Assuming the intensity of radiant energy from a flame is proportional to its temperature, it should be possible to measure the *relative* temperature of the flame. Of course, it was necessary to maintain a constant distance between the edge of the flame and the thermistor.

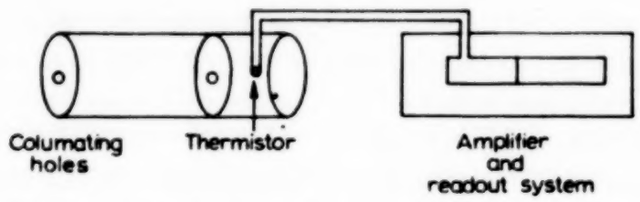

Fig. 4. Diagram of instrument for comparing flame temperature.

One advantage of this instrument is that the temperature of a small part of the flame is taken. This made it possible for a profile of the flame temperature to be obtained, and enable the maximum flame temperature to be used for comparative purposes, rather than the average flame temperature which is obtained with other techniques.

In practice it was found that a base line drift occurred caused by heating of the instrument because it was in close proximity to the flame. This problem was overcome by alternately inserting and removing a shield between the flame and the inlet of the columator and measuring the deflection obtained in the readout. This deflection is proportional to the change in temperature of the thermistor on exposure to the flame, and is therefore a function of the flame temperature. For this work, absolute flame temperatures were not measured since it was only necessary to ensure that the non-stoichiometric flames were equal in temperature.

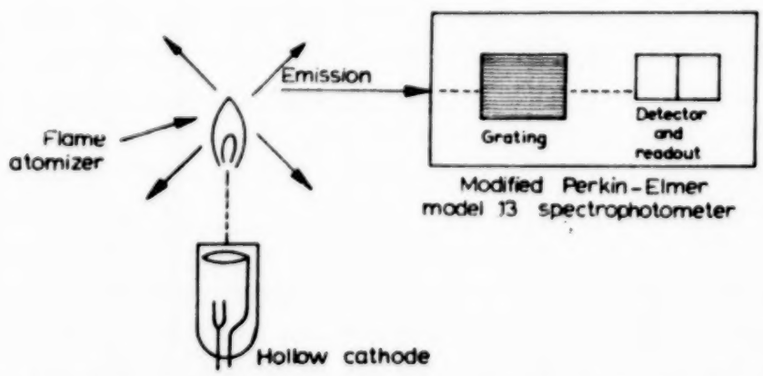

Fig. 5. Equipment used for external excitation of metal spectra.

Excitation using an external source of U.V. light

If, as has been postulated, spectra can be generated by U.V. light, it should be possible to use an external source of U.V. light to generate spectra. This was examined experimentally in the following manner.

Equipment: A schematic diagram of the equipment is shown in Fig. 5.

An aqueous solution of a suitable metal was aspirated into a standard Beckman flame photometer burner. The spectrophotometer was arranged such that the de-

tector continuously monitored the resonance line of the metal being examined. A hollow cathode was positioned at right angles to the light path of the flame and the slit of the spectrophotometer. The intensity of the emission was measured (*a*) with the hollow cathode on and (*b*) with it off. If excitation of the metal atoms in the flame occurs, there should be enhancement of the strength of the spectral line. Of course, it will be appreciated that the metal atoms will absorb the U.V. light and re-emit at random, forming a solid sphere of radiant energy. The slit sees a very small part of this solid angle and therefore only a very small portion of the re-emitted light would be utilized. To detect this small amount of energy, the instrument was run at maximum sensitivity. The results obtained were as follows:

Sodium. λ 5890 Å. No enhancement of intensity was detected. However, it was noted that the intensity of the flame emission signal was so high that it would be very difficult to detect the small enhancement expected.

Nickel. λ 3524.5 Å, 3414 Å. No enhancement was detected. In this case the oscillator strength of these spectral lines is low. This would mean that the nickel would be very inefficient in absorbing energy from the hollow cathode. As a result, only a small amount of energy would be re-emitted.

Magnesium. λ 2852 Å. The results obtained with magnesium are shown in Fig. 6.

The Mg 2852 Å line gave good conditions for detection of 'fluoresced' light. The oscillator strength of the line is high. This permits efficient absorption of energy from the hollow cathode. Further, the original emission intensity is low, allowing the instrument to be set at high sensitivity. Under these conditions, any re-emitted signal

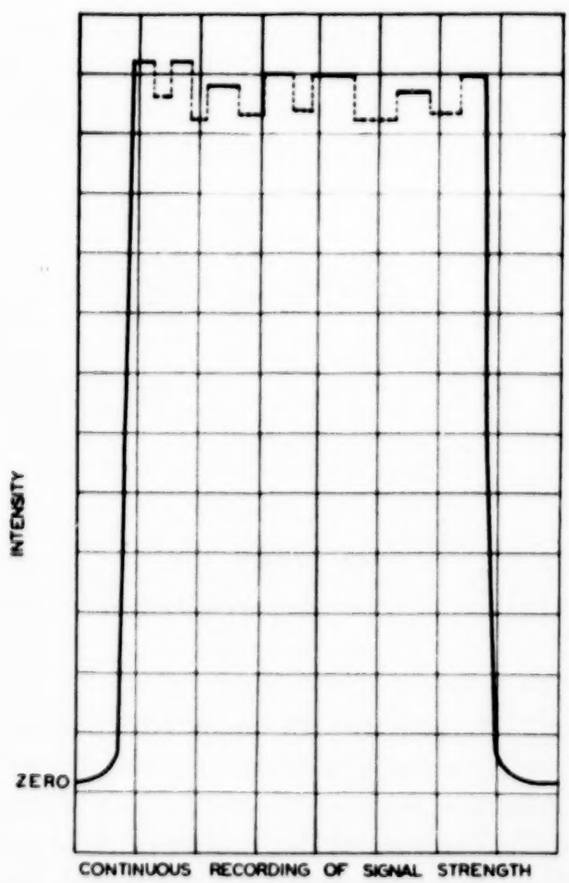

Fig. 6. Enhancement of Mg 2852 Å line using a hollow cathode. ——— Mg (1000 p.p.m.) with hollow cathode; – – – – Mg (1000 p.p.m.) without hollow cathode.

was significant compared to the emission of the metal excited by the flame alone. This allowed a significant measurement of 'fluoresced' light to be made.

It appears from Fig. 6 that some enhancement of the signal occurred. Care was taken to prevent reflected light from the hollow cathode reaching the extrance slit of the monochromator. Further, since there was no enhancement detected in the case of sodium and nickel, it can be assumed that the reflection from the flame, or droplets in the flame, was negligible since such reflections would have caused an apparent signal in the case of these two metals.

Attempts to use a continuous source of radiation (hydrogen lamp) to cause "fluorescence" were unsuccessful. Although the total quantity of energy was much greater than that in the flame, the quantity of energy from the lamp having the correct wavelength was small. Atomic absorption indicates that absorption lines are of the order of 0.03 Å wide. This indicates that the source must not only be of sufficient energy to excite the metal atoms, but must be of the correct wavelength. A hollow cathode is a much better source of such radiation since the wavelength and intensity requirements are met more favorably. It is also important to remember that with external excitation, the atom is subjected to radiant energy coming from one direction only. However, in the environment of a flame, that atom is at the center of a sphere of radiation from the flame. Further, this radiant energy is in very close proximity compared to an external source. It can be seen, therefore, that the intensity of U.V. light in the flame is considerable greater than would be suspected from a simple measurement of its emission intensity at the wavelength considered because (*a*) the atom is at the center of a sphere of radiant energy, (*b*) the energy source is infinitely close to the atom. Both these advantages are lost with an external source.

RESULTS

The results indicated strong evidence that ambient U.V. light contributed to the intensity of the metal spectra emitted from flames. Further, it seems reasonable to conclude that we can project these results to emission spectrography.

It is well known that the strength of a metal emission line obtained from a spectrograph is modified by the matrix of the sample and by the interelement effects of elements other than the matrix. Of course, the matrix will control to some extent the volatility of the metal being examined, but it is also possible that U.V. emission from the matrix will further excite this metal if the wavelength relationship is suitable. On the other hand, of course, it is possible that the matrix absorbs light emitted by the sample metal. This would result in considerable loss of intensity of emission, depending on the ratio of metal to matrix. In conventional spectrography, great pains are taken to keep this ratio constant by laying down the sample on a standard matrix.

The same modifications of spectral intensity may also be produced by other elements present in the sample, *i.e.*, enhancement by excitation, depression by absorption. Normally, this interelement effect is hard to control because the elements in question are often impurities in the matrix, or the sample, and only extensive purification procedures eliminate the difficulty.

Although this suggestion does not solve the problem of imprecision in spectrography, it does help to understand them, and this understanding may lead to a solution at a later date.

SECONDARY EFFECT OF U.V. LIGHT

As described elsewhere[1], it is probable that a metal becomes a hydrate and/or an oxide before breaking down to the atomic state. This process is important in controlling the number of excited atoms produced in a flame, and hence the intensity of emission. Metal hydrates and oxides usually exhibit broad band spectra and conversely it may be expected that they would absorb energy over a similar broad wavelength band. If intense U.V. light is present in the source at these wavelengths, it is probable that much of this energy is absorbed and that it contributes to the breakdown of the molecules, releasing free atoms.

This would result in an increase in the number of excited metal atoms formed, and therefore in the intensity of the spectra they emit. Under these conditions the U.V. light would not be exciting the atoms directly as with the hollow cathode, but would be increasing the efficiency of producing the emitting species. The net effect would be an increase in spectral intensity.

CONCLUSIONS

It is concluded from these observations that the intensity of a metal emission spectrum is dependent on the following variables:

1. *Flame temperature.* The equations listed above indicate the temperature/emission intensity relationship.

2. *U.V. light generated in the flame.* Both the wavelength and intensity of this light are important in exciting atoms.

3. *Mechanism of producing atoms.* This controls the number of ions or molecules which will be reduced to atoms by passage through a flame. Solvent and U.V. light affect the efficiency of this step.

4. *Absorption of U.V. light* by solvents or fragments of solvents present in the flame. This would result in a depression of line intensity.

ACKNOWLEDGEMENT

The author wishes to thank Esso Standard, Division of Humble Oil & Refining Company, for permission to publish this paper.

SUMMARY

It is generally believed that emission spectra result from thermal excitation. It is proposed that ultraviolet light present in a flame is also responsible for exciting metal atoms present. Experimentally it has been shown that the intensity of metal emission spectra is a function of the U.V. characteristics of the flame even at constant flame temperature. It was also demonstrated that spectral intensity can be enhanced by external radiation of U.V. light of the correct wavelength.

RÉSUMÉ

L'auteur a étudié le mécanisme de l'excitation spectrale en photométrie de flamme, montrant que les spectres d'émission ne sont pas dus seulement à une excitation thermique, mais aussi aux radiations ultra-violettes.

ZUSAMMENFASSUNG

Es wird nachgewiesen, dass Emissions Spektren nicht allein durch thermische Anregung entstehen, sondern dass die Intensität der Metall Emissionsspektren durch die ultravioletten Strahlen der Flamme stark beeinflusst wird.

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SPECTROPHOTOMETRIC STUDY OF THE BERYLLIUM–THORIN COMPLEX AND ITS APPLICATION TO THE DETERMINATION OF BERYLLIUM IN ALLOYS

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Azo dyes substituted in the *o*-position to the azo linkages combine with certain metallic ions to form characteristic closed ring compounds and these dyes can be made specific for a particular group of metals by having a functional group in the *o*-position which reacts preferentially with this group of metals[1].

In the investigation of such a compound, 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulfonic acid (thorin), for the determination of thorium, BYRD AND BANKS[2] reported that beryllium causes interference if the ratio of $BeO:ThO_2$ is 2000:1. ADAMOVITCH AND YUTSIS[3] have utilised the reaction of beryllium with thorin for the determination of beryllium in ferrous alloys.

The present paper deals with the nature and the optimum conditions for the formation of the beryllium complex with thorin and its application to the determination of beryllium in different beryllium alloys.

EXPERIMENTAL

All absorption measurements were made on a Beckman DU spectrophotometer using 1-cm pyrex cells.

Reagents

Standard beryllium chloride solution. This was prepared from pure BeO (Merck) and standardised. Aliquots of the stock solution were diluted to give $2 \cdot 10^{-4}$ *M* Be solutions.

Thorin solution. Thorin supplied by Eastman Kodak (White Label) was purified by recrystallization. The purity was determined by potentiometric titration[4] and was found to be 98% (Fig. 1). This purified reagent was used throughout the work.

Optimum pH and wavelength

Aliquots containing 10 μg of beryllium were treated with excess thorin in 25-ml volumetric flasks, the pH of the solutions being varied from 1 to 13. The absorption spectra of these solutions measured against reagent blanks showed maximum absorbance at pH 12 and at 470 mμ.

Beryllium–thorin complex

The formula of the complex was determined by various methods.

(*a*) *Job's method of continuous variation*[5,6]. The spectra of solutions with the ratios of reagent to metal 1:1, 2:1 and 3:1 were measured against reagent blanks. No isobestic points were observed, thus the formation of a single complex with maximum absorbance at 470 mμ at pH 12 was indicated. Fig. 2 indicates the results obtained at 470 and 530 mμ, the pH being adjusted to 12 by borate–sodium hydroxide buffer. Only a 1:1 complex is indicated.

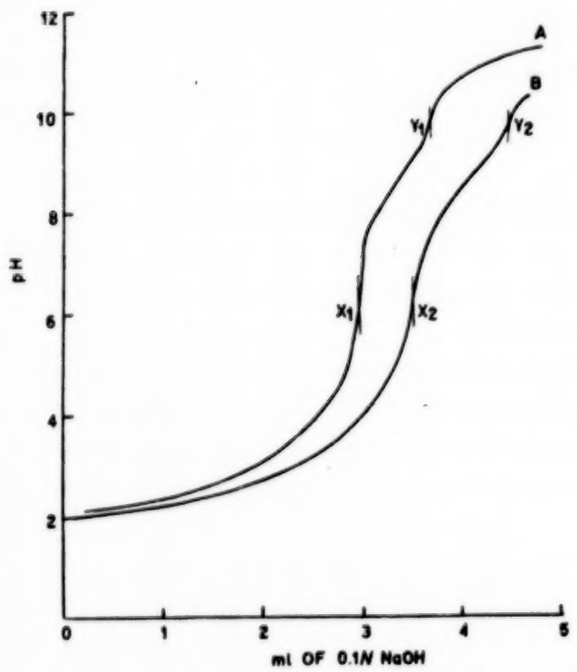

Fig. 1. Potentiometric titration of 10 ml 0.01 *M* Thorin. A: before purification; B: after purification. $x_1, y_1 = 0.75$ mequiv., A = 75% pure; $x_2, y_2 = 0.98$ mequiv., B = 98% pure.

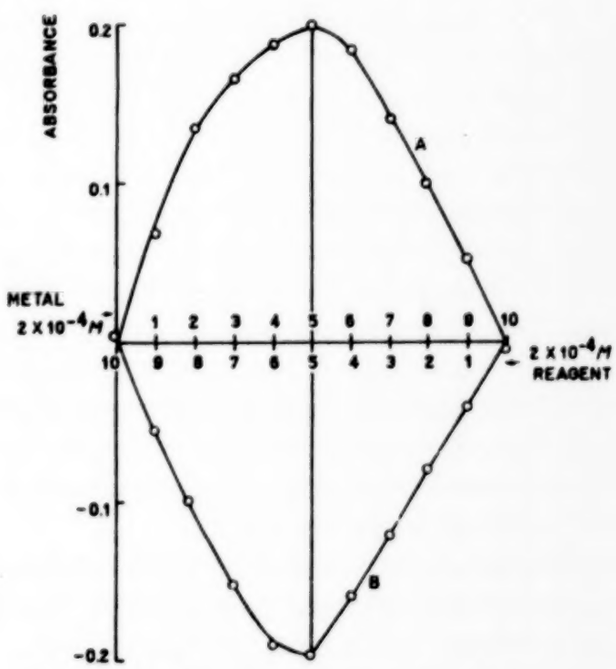

Fig. 2. Continuous variation. A: at 470 mμ; B: at 530 mμ.

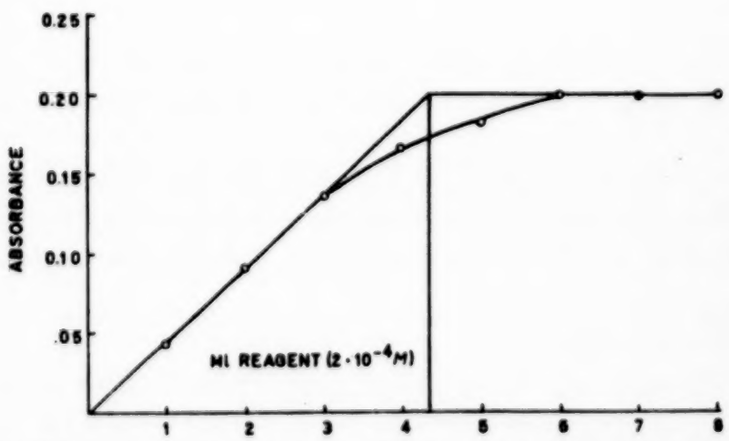

Fig. 3. Mole ratio method. Metal ion concentration 4 ml of $2 \cdot 10^{-4}$ *M*

(*b*) *Mole ratio method*[7]. The results obtained (Fig. 3) indicate the formation of a 1:1 complex. The measurements were made at 470 mμ and at pH 12.

(*c*) *Slope ratio method*[8]. The composition of the complex was also checked by the slope ratio method. Measurements were made at 470 mμ for solutions adjusted to pH 12 with sodium hydroxide–borate buffer. A 1:1 complex was clearly indicated (Fig. 4). All the methods show that 1:1 complex is formed between beryllium and thorin.

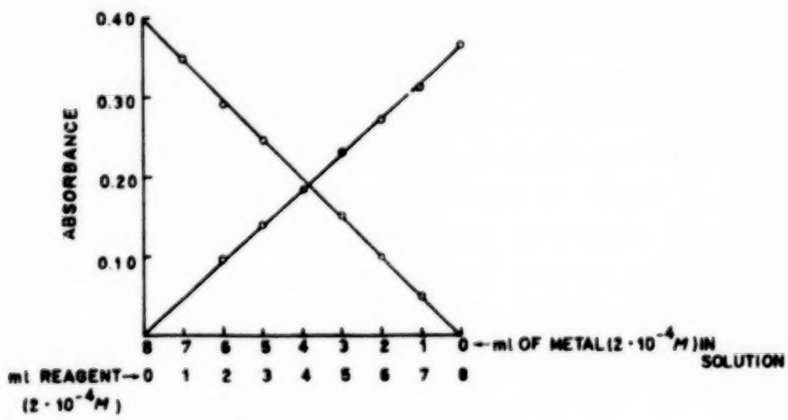

Fig. 4. Slope ratio method.

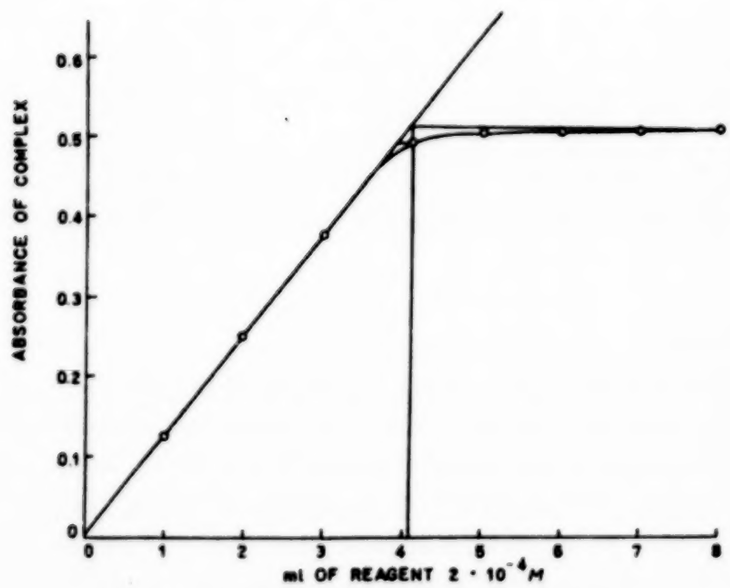

Fig. 5. Approximate dissociation constant.

Dissociation constant

By the method of STEARNS[9] the approximate dissociation constant of the complex was calculated. Aliquots of 4 ml of $2 \cdot 10^{-4}$ *M* thorin were placed in 25-ml flasks and $2 \cdot 10^{-4}$ *M* beryllium solution was added in amounts varying from 0 to 8 ml (2 equivalents). The solutions were diluted to 25 ml with buffer of pH 12, and the absorbancies were measured at 470 mμ (Fig. 5). An approximate value of the dissociation constant was calculated from the above data. From this value the amount of free reagent formed by dissociation and hence its absorbance was calculated. This was subtracted

from the total absorbance to give the absorbance due to the complex and the dissociation constant was again calculated. Similar successive approximations were made till a constant value for the dissociation constant, $1.38 \cdot 10^{-7}$, was obtained.

Determination of beryllium in alloys

Beryllium alloyed with other metals like Cu, Ni, Fe, Zn, Al etc., confers certain desirable properties on these alloys. The percentage of beryllium usually varies from 0.05% to 2.0%. Thorin cannot, however, be used directly for the determination of beryllium in these alloys since metals like Ca, Mg, Fe, etc., interfere. Acetylacetone forms well-defined chelates with a number of metals including beryllium. Many of these chelates are highly soluble in organic solvents so that macro and micro separations are feasible[10]. If EDTA is used as masking agent a basis is found for the separation of beryllium as acetylacetonate from other metals like Fe, Al, Zn, Cu, Cr, etc.[10]. The procedure thus evolved for the separation of beryllium before its determination is described below.

Standard beryllium solutions of strength 1 ml = 100 μg and 1 ml = 10 μg were prepared from the stock solution.

Standard curve

Standard beryllium solutions containing 1–10 μg of beryllium were placed in 25-ml volumetric flasks and 2 ml of aqueous 0.1% thorin solution was added. The solutions were diluted to 25 ml with sodium hydroxide–borate buffer to give a final pH of 12. The optical densities of the solutions were measured at 470 mμ against a reagent blank on a Beckman DU spectrophotometer using 1-cm pyrex cells. Standards were also taken for the 20–100 μg range of beryllium using 10 ml of 0.1% thorin, the final volume in this case being 100 ml. The results show that Beer's law is obeyed in both cases.

Procedure for samples

To about 10 ml of solution containing 1–100 μg of beryllium, 5 ml of aqueous 10% EDTA was added. The pH was adjusted to 4–5 by the addition of dilute ammonia using pH indicator paper. One ml of aqueous 15% (v/v) acetylacetone was added followed by two drops of concentrated ammonia to bring the pH between 7 and 8 as seen by pH indicator paper. The solution was allowed to stand for 5 min and then shaken with 5 ml of carbon tetrachloride for 7 min. The organic layer was transferred to another clean separating funnel. The extraction was repeated thrice with fresh 5-ml portions of carbon tetrachloride after adding 1.0 ml of acetylacetone each time.

The combined organic layers were shaken for 7 min with 3 ml of concentrated hydrochloric acid diluted to 7 ml with water and the organic phase was then rejected. The aqueous phase was evaporated to dryness and fumed with perchloric acid. The residue was taken up in a little water, thorin added and the pH adjusted to 12 using borate–sodium hydroxide buffer. The absorbance was measured at 470 mμ against a reagent blank.

Table I shows the optical densities obtained with thorin for beryllium solutions (1) taken through the procedure and (2) by direct development of colour; these agree well.

TABLE I

Be in μg	*Optical density with thorin*				
	Directly			*Through procedure*	
per 25 ml					
1	0.029	0.028	0.029	0.029	0.030
2	0.055	0.059	0.059	0.058	0.060
3	0.085	0.090	0.085	0.082	0.087
4	0.112	0.110	0.115	0.110	0.114
5	0.144	0.140	0.145	0.143	0.145
6	0.177	0.175		0.171	0.175
8	0.230	0.235		0.230	0.232
10	0.295	0.300		0.290	0.295
per 100 ml					
25		0.180	0.177	0.178	0.185
50		0.355	0.365	0.355	0.360
75		0.530	0.520	0.525	0.515
100		0.720	0.710	0.712	0.730

Determination of beryllium in Cu–Be alloys

0.1072 g of the alloy was dissolved in dilute nitric acid, evaporated to dryness and diluted to 250 ml with distilled water. A 10-ml aliquot was transferred to a separating funnel and beryllium was separated by the above procedure. The colour was developed with 10 ml of 0.1% thorin in a final volume of 100 ml at pH 12 and its absorbance was measured against a reagent blank at 470 mμ. In order to see whether the recovery of beryllium was quantitative, a standard beryllium solution was added to another 10-ml aliquot and beryllium estimated. The results are shown in Table II. The percentage of Be in the sample was also checked by a gravimetric procedure[11] and was found to be 1.93; this is in good agreement with the values obtained by the present method.

TABLE II

Amount of Cu–Be alloy taken in mg	*Amount of Be added in μg*	*Amount of Be found in μg*	*% Be*
4.288	Nil	79.31	1.85
4.288	Nil	80.00	1.86
4.288	Nil	77.90	1.82
4.288	10	88.7	
4.288	10	89.6	

Determination of beryllium in other alloys

Beryllium is also a constituent of ferrous and non-ferrous alloys. The compositions of these alloys are given in Table III. Synthetic alloy solutions were prepared by taking beryllium and other metals in the respective proportions as nitrates. As chlorides, nitrates or sulphates do not interfere with the extraction of beryllium as acetylacetonate, any of these acids can be utilised for the dissolution of the alloy. Aliquots containing 10 mg of the alloys were taken and beryllium was determined as described above.

Determination of beryllium in steel

Recoveries were also carried out after addition of a known amount of beryllium to a stainless steel solution. 0.1 g of a high speed steel (British Chemical Standard

TABLE III

Description of alloy	*Composition of synthetic alloy mixture*	*Beryllium found* %
Be-Cu alloy	0.5% Be 1.5% Co 0.7% Ni 1.0% Ag 96.3% Cu	0.483 0.482 0.475 Mean: 0.48
Ferrous alloy[a]	0.05% Be 15.00% Ni 20.00% Cr 7.00% Mo 32.00% Co 8.00% W 2.00% Mn 15.95% Fe	0.049 0.046 0.048 0.048 Mean: 0.048
Ferrous alloy[b]	0.8% Be 50.0% Ni 49.2% Fe	0.75 0.77 0.75 Mean: 0.76
Zinc base alloy	0.1% Be 2.2% Cu 97.7% Zn	0.097 0.098 0.10 Mean: 0.098
Light alloy	0.2% Be 5.0% Mg 1.0% Si 0.3% Mn 0.15% Ti 93.35% Al	0.18 0.18 0.20 Mean: 0.19

[a] In the case of the alloy containing tungsten, tungstic acid is precipitated when the alloy is treated with acid, but on addition of EDTA and then NH_4OH, it goes into solution as ammonium tungstate at pH 6–7. An aliquot of this solution was taken and after addition of 1 ml of acetylacetone, beryllium was estimated in the usual way.

[b] For the alloy containing a high percentage of iron, it is necessary to repeat the extraction of beryllium as acetylacetonate from the first acid extract to ensure complete removal of iron.

No. 241) of the composition given in Table IV was dissolved in 2 ml of 1 : 1 hydrochloric acid and the carbon was oxidised by the addition of a few drops of nitric acid. A solution equivalent to 50 μg of beryllium was then added followed by 50 ml of 10% EDTA and then ammonia (1 : 1) till the solution became clear. It was then diluted to 100 ml. 10 ml of the solution was pipetted out into a separating funnel and 1 ml of acetylacetone was added. The pH was brought to 7–8 by addition of dilute ammonia and extractions were carried out with carbon tetrachloride. After the beryllium had been extracted into acid, the acetylacetonate extractions were repeated to ensure complete removal of iron. The results (Table IV) show that the method can be applied to the determination of beryllium in its alloys.

TABLE IV

Composition of sample BCS No. 241 (High speed steel)	*Total Be added in μg*	*Be found in μg*	*Recovery %*
W = 6.74% Mo = 4.17% Cr = 4.61% V = 1.35% Co = 0.67% C = 0.86% Si = 0.30% S = 0.039% P = 0.024% Mn = 0.25% Ni = 0.15% Cu = 0.14% Sn = 0.04%	50	47	94
	50	48	96

SUMMARY

A spectrophotometric study of the beryllium complex with purified thorin shows the formation of a 1 : 1 complex at pH 12. The dissociation constant obtained after successive corrections for reagent absorbance is $1.38 \cdot 10^{-7}$. Beryllium in concentrations of 0.05% to 2.0% in copper base, zinc base, aluminium base and ferrous alloys can be determined by the formation of the thorin complex after its preliminary separation as acetylacetonate in presence of EDTA.

RÉSUMÉ

Les auteurs ont effectué une étude spectrophotométrique sur le complexe béryllium–thorin. Des méthodes sont décrites pour le dosage du béryllium dans ses alliages.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Bestimmung von Beryllium in seinen Legierungen mit Hilfe von Thorin.

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SPEKTROPHOTOMETRISCHE BESTIMMUNG VON NIOB MIT ASCORBINSÄURE

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(Eingegangen den 22. August 1960)

Ascorbinsäure wurde schon früher von HINES UND BOLTZ[1] sowie KORKISCH UND FARAG[2] zur spektrophotometrischen Bestimmung von Titan, mit dem sie einen gelben Komplex bildet, verwendet. Sie bildet auch mit Niob eine gelbgefärbte Verbindung, die in demselben Wellenlängenbereich wie der Titanascorbinatkomplex maximale Extinktion aufweist. Da das Beersche Gesetz über einen weiten Konzentrationsbereich gilt und die Handhabung der Methode relativ leicht ist, weist die hier beschriebene gegenüber den üblichen Methoden zur photometrischen Bestimmung des Niobs[3] nicht zu unterschätzende Vorteile auf.

LÖSUNGEN UND REAGENTIEN

Niob- und Tantalstandardlösungen

0.1969 g Nb_2O_5 wurden zusammen mit 5 g wasserfreiem Kaliumcarbonat eine halbe Stunde lang in einem Platintiegel geschmolzen, die Schmelze abkühlen gelassen und schliesslich in insgesamt 100 ml Wasser gelöst. Diese carbonat-alkalische Niobatlösung enthielt 1 mg Nb/ml. Auf analoge Weise wurde eine Tantalatlösung durch Schmelzen von 0.1222 g Ta_2O_5 hergestellt, die 1 mg Ta/ml enthielt. Durch entsprechendes Verdünnen mit dest. Wasser wurden aus diesen Stammlösungen Lösungen mit geringeren Niob- bezw. Tantalgehalten hergestellt.

Ascorbinsäurelösung

Unter Verwendung von reiner Ascorbinsäure der Wiener Heilmittelwerke wurde eine 10%-ige Lösung dieser Säure in dest. Wasser hergestellt. Diese Lösung muss allerdings immer unmittelbar vor ihrer Verwendung frisch bereitet werden und in vielen Fällen ist die Verwendung fester Ascorbinsäure vorzuziehen.

Ferner wurden angewendet

Standardlösungen einer Anzahl von Fremdionen (s. Tab. II), 4 *N* und 1 *N* Salzsäure, 2.5 *M* Natriumacetatlösung sowie wasserfreies Kaliumcarbonat *p.a.*

APPARATE

Die photometrischen Messungen wurden mit einem Beckmann Spektrophotometer, Modell B, bei einer Wellenlänge von 345 mμ in 1-cm Küvetten ausgeführt.

ABHÄNGIGKEIT DER EXTINKTION VON DER WELLENLÄNGE

1 ml einer Niobatlösung, die 200 μg Nb/ml enthielt, wurde mit 5 ml 10%-iger Ascorbinsäure, 1 ml 2.5 *M* Natriumacetatlösung und 0.6 ml 1 *N* Salzsäure in einem 10-ml Messkolben mit dest. Wasser zur Marke aufgefüllt und die Extinktion dieser Lösung im Wellenlängenbereich von 310 bis 410 mμ gegenüber einer analog hergestellten Reagensleerlösung gemessen. Die Ergebnisse dieser Messungen sind aus Tabelle I ersichtlich. Daraus ist zu entnehmen (Spalte 2) dass das Maximum der Extinktion bei einer Wellenlänge von 345 mμ liegt.

TABELLE I

Wellenlänge in mμ	*Extinktion von Niob*	*Extinktion von Tantal*
310	0.065	0.015
320	0.220	0.140
325	0.330	0.190
330	0.385	0.200
335	0.400	0.185
340	0.415	0.160
345	0.420	0.145
350	0.410	0.120
360	0.385	0.085
370	0.340	0.060
380	0.310	0.040
390	0.280	0.030
400	0.230	0.020
410	0.145	0.010

Analoge, in einem 50-ml Messkolben durchgeführte, Messungen bei denen 1 mg Niob, 25 ml 10%-ige Ascorbinsäure, 5 ml 2.5 *M* Natriumacetatlösung und die zur Neutralisation der carbonatalkalischen Lösung erforderliche Menge an verdünnter Salzsäure (*vide infra*) angewendet wurden, ergaben Resultate, die mit den in Spalte 2 angegebenen identisch waren.

In Spalte 3 der Tabelle I sind die Ergebnisse der unter völlig gleichen Bedingungen mit Tantal ausgeführten Messungen wiedergegeben. Daraus geht hervor, dass das Maximum der Tantalextinktion bei 330 mμ liegt.

EINFLUSS DER SALZSÄUREKONZENTRATION

Die optimale Salzsäuremenge variiert natürlich mit dem Carbonatgehalt der Stammlösung. Beim Arbeiten in 10-ml Messkolben nach Aufschluss einer Niobpentoxydmenge von 0.1969 g mit 5 g Kaliumcarbonat wurde bei einem konstanten Gehalt von 3 ml 10%-iger Ascorbinsäurelösung, 1 ml 2.5 *M* Natriumacetatlösung und einem aliquoten Teil der verdünnten Niobatlösung, der 200 μg Niob enthielt, die in Fig. 1 gezeigte Kurve erhalten. Da bei Anwendung von 0.3 bis 1.0 ml 1 *N* Salzsäure praktisch immer dieselbe Extinktion erzielt wurde, wird demnach im Weiteren nur mehr das in der Mitte des Konstanzbereiches liegende Volumen von 0.6 ml 1 *N* HCl/10 ml Messlösung bei sonst gleichen Bedingungen verwendet und damit im Konzentrationsbereich von 10–400 μg Niob eine lineare Abhängigkeit der Extinktion von der Konzentration erhalten.

Beim Arbeiten in 50-ml Messkolben und mit wechselnden Carbonatgehalten der Niobatlösung wird die erforderliche Salzsäuremenge folgendermassen ermittelt: 10 ml der Stammlösung, die durch Ausziehen des Aufschlussgutes (0.1–1.0 g Substanz mit bis zu 10 g Kaliumcarbonat) mit 100 ml dest. Wasser erhalten wird, werden mit 1 *N*

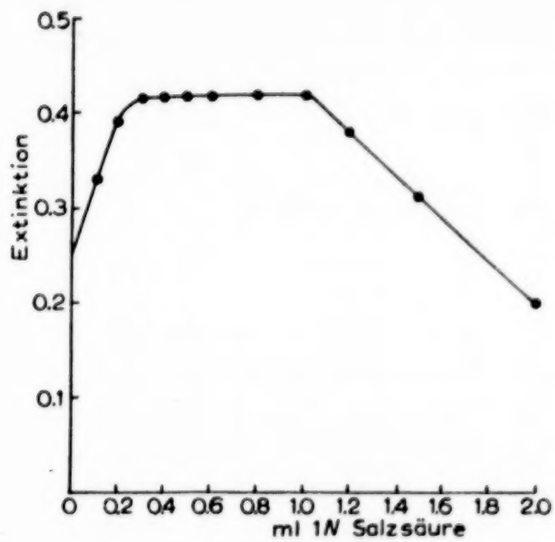

Fig. 1. Einfluss der Salzsäurekonzentration.

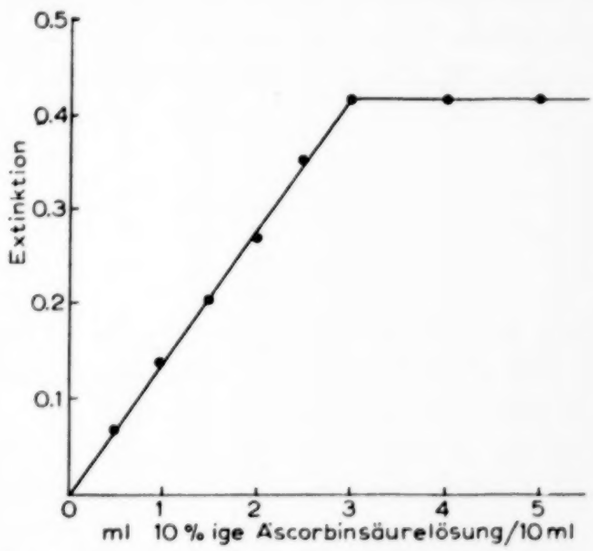

Fig. 2. Einfluss der Ascorbinsäurekonzentration.

Salzsäure unter Verwendung von Phenolphthalein als Indikator auf farblos titriert. Wenn *a* ml der 1 *N* Salzsäure verbraucht wurden, so muss pro ml der Stammlösung eine Menge von $x = a \cdot 0.6$ ml 4 *N* Salzsäure bzw. die vierfache Menge 1 *N* HCl/50 ml Messlösung zugesetzt werden. Es wurden Messlösungen mit Gehalten von 2.5–25 ml einer 10%-igen Kaliumcarbonatlösung und Niobgehalten von 500 und 1000 μg Nb/50 ml mit der ermittelten Salzsäuremenge versetzt und die so erhaltenen Ergebnisse stimmten innerhalb von $\pm$ 4.0% überein.

EINFLUSS DER ASCORBINSÄUREKONZENTRATION

Wie aus Fig. 2 hervorgeht wird die maximale Extinktion schon bei Anwesenheit von 3 ml der 10%-igen Ascorbinsäurelösung/10 ml Messlösung erreicht, doch haben wir später immer einen Überschuss und zwar 5 ml der 10%-igen Ascorbinsäurelösung bzw. 0.5 g feste Ascorbinsäure/10 ml zugesetzt, wodurch etwa vorhandene Manganationen reduziert werden können, ohne dass die Ascorbinsäurekonzentration dabei praktisch abnimmt.

EINFLUSS VON TEMPERATUR UND ZEIT

Da die Anwesenheit des aus dem Carbonat in Freiheit gesetzten Kohlendioxydes in der Messlösung eine reproduzierbare Messung unmöglich machen würde, haben wir auf verschiedene Weise versucht diesen Einfluss auszuschalten. Am besten ist es, das Kohlendioxyd aus den Lösungen mit Unterdruck abzusaugen. Nach einstündigem Evakuieren im Vakuumexsikkator mit einer gut ziehenden Wasserstrahlpumpe ist alles überschüssige Kohlendioxyd abgesaugt (es steigen keine Blasen mehr auf). Nach

dem Auffüllen und mehrmaligen Umschütteln wird der Messkolben mit Leitungswasser auf eine Temperatur von 15 bis 20° gebracht, da die Extinktion zwischen 12 und 20° praktisch konstant ist. Oberhalb 20° fällt sie ab und geht bei Temperaturen über 40° rasch gegen Null. Nach Ablauf von 10 min wird dann die Extinktion gemessen und verändert sich während der nächsten 30 min um höchstens 2.0%. Hierauf beginnt sie zuerst langsam, dann etwas schneller abzunehmen.

GÜLTIGKEIT DES BEERSCHEN GESETZES

Die Lösungen enthielten von 0 bis 50 μg Nb oder Ta/ml. Beim Arbeiten in 10-ml Messkolben gilt das Beersche Gesetz im Konzentrationsbereich von 2–40 μg Nb/ml, beim Arbeiten in 50-ml Kolben von 0.5 bis 40 μg/ml Messlösung. An Reagentien waren in den 10-ml Messkolben: 0.5 g Ascorbinsäure, 1 ml der 2.5 M Natriumacetatlösung und 0.6 ml 1 N Salzsäure sowie 0–500 μg Niob oder Tantal mit der entsprechenden Carbonatmenge (bzw. nach der Säurezugabe Kaliumchlorid) enthalten. In den 50-ml Messkolben waren 2.5 g Ascorbinsäure, 0–2500 μg Niob oder Tantal + Kaliumcarbonat, 5 ml der 2.5 M Natriumacetatlösung und die berechnete Salzsäuremenge zugegen. Die Extinktion wurde für Niob bei 345 mμ (Kurve I) und 360 mμ (Kurve II), für Tantal bei 330 mμ (Kurve III) und 360 mμ (Kurve IV) gemessen (s. Fig. 3).

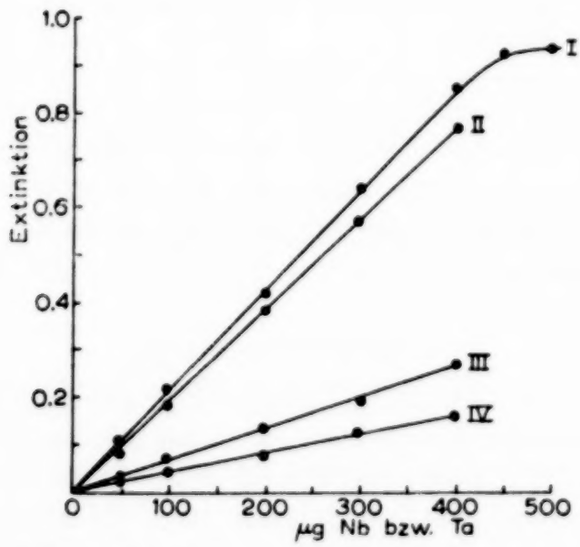

Fig. 3. Gültigkeit des Beerschen Gesetzes.

Wie aus den Kurven III und IV ersichtlich ist, lässt sich Tantal ebenfalls mit Ascorbinsäure photometrisch bestimmen, wobei aber die Messgenauigkeit infolge der ungenügenden Steilheit der Eichkurve relativ gering ist.

EMPFINDLICHKEIT DER METHODE UND EINFLUSS DER REAGENTIENZUGABE

2–40 μg bzw. 0.5–40 μg Nb/ml sind noch bestimmbar. Der prozentuelle Fehler beträgt $\pm$3–4%. Die Reihenfolge der Reagentienzugabe ist ohne Einfluss, doch ist es günstiger die Ascorbinsäure zuerst in den trockenen Messkolben einzuwägen.

EINFLUSS VON FREMDIONEN

In Tabelle II wird der Einfluss einer Reihe von Fremdionen gezeigt.

TABELLE II

Eingesetzte Niobmenge in µg	*Gleichzeitig anwesendes Fremdion*	*Wiedergefundene Niobmenge in %*
200	1 mg Kaliumphosphat	73.0
200	2 mg Natriumsulfat	99.0
200	0.1 g Kaliumchlorid	100.0
200	1 mg Kaliumjodid	102.5
200	1 mg Kaliumbromid	62.0
200	0.1 g Kaliumnitrat	96.0
200	1 mg Natriumfluorid	27.0
200	200 µg Ammoniumbichromat	104.0
200	200 µg Uranylchlorid	140.0
200	200 µg Aluminiumchlorid	118.0
200	200 µg Vanadium als Vanadat	169.0
200	200 µg Molybdän als Molybdat	135.0
200	200 µg Wolfram als Wolframat	110.0
200	200 µg Nickel als Chlorid	112.0
200	200 µg Cobalt als Chlorid	120.0
200	200 µg Mangan als Manganat	108.0
200	1 ml 0.1 *M* ÄDTA-Lösung	10.0
200	100 µg Tantal	115.0
200	200 µg Tantal + 1 ml 0.1 *M* ÄDTA-Lösung	0.0
200	100 µg Titan	190.0

Man sieht aus den Eichkurven I und III, dass eine Menge von 20% Tantal (bezogen auf Niob) einen Fehler von +8% verursacht. Misst man jedoch die Extinktion bei 360 mµ (Eichkurven II und IV) anstatt bei 345 mµ, so verursachen erst *ca.* 40% Tantal den gleichen Fehler.

ARBEITSVORSCHRIFT

(*a*) Für Niobgehalte von 0.5 bis 8% und darüber bei einer Einwaage von 0.5 g der Probe oder weniger nach 1/2 stündigem Aufschluss mit 5 g Kaliumcarbonat.

Das Schmelzgut wird mit insgesamt 100 ml dest. Wasser aufgenommen und dabei gleichzeitig in einen 100-ml Messkolben gebracht. 1 ml dieser, oder 1 ml einer entsprechend mit dest. H_2O verdünnten Lösung, die insgesamt 20–400 µg Nb/ml enthalten soll, wird in einen 10-ml Messkolben gebracht, in den vorher 0.5 g Ascorbinsäure eingewogen worden waren. Hierauf wird 1 ml der 2.5 *M* Natriumacetatlösung, 0.6 ml 1 *N* Salzsäure und etwas dest. Wasser zugesetzt, sodass der Kolben etwa halbvoll ist. Die Messlösung wird dann zusammen mit der Leerlösung, die ebenfalls 0.5 g Ascorbinsäure und 1 ml der Natriumacetatlösung aber keine Salzsäure im halbvollen Kolben enthält, in einen Vakuumexsikkator gestellt und eine Stunde lang mit einer Wasserstrahlpumpe evakuiert. Anschliessend werden die Kolben herausgenommen, mit dest. Wasser aufgefüllt, mehrmals umgeschüttelt und mit Leitungswasser auf gleiche Temperatur gebracht. Nach Ablauf von 10 min wird dann die Messung ausgeführt. Die Extinktion bleibt nahezu 30 min lang konstant.

(*b*) Für Gehalte von 0.01–4.0% bei einer Einwaage von 0.1–2 g Probe nach 1/2 stündigem Aufschluss mit 10 g Kaliumcarbonat.

Der erkaltete Schmelzkuchen wurde dann wie unter (*a*) beschrieben weiter be-

handelt. Der 100 ml betragenden Lösung werden 10 ml entnommen, auf 50 ml verdünnt und unter Verwendung von Phenolphthalein als Indikator mit 1 *N* Salzsäure kalt auf farblos titriert, wodurch ein Verbrauch von *a* ml erhalten wird. In ein 150-ml Becherglas werden 2.5 g Ascorbinsäure eingewogen und mit 5 bis 25 ml der niobhaltigen Lösung, die insgesamt 25 bis 2000 μg Niob enthalten sollen, versetzt. Hierauf werden 5 ml der 2.5 *M* Natriumacetatlösung und $a \cdot 0.6$ ml 4 *N* bzw. $a \cdot 2.4$ ml 1 *N* Salzsäure mal der Anzahl der ml an zugesetzter Probelösung zugegeben, das Becherglas mit einem Uhrglas bedeckt und in den Vakuumexsikkator gebracht. Eine Lösung bestehend aus 2.5 g Ascorbinsäure, 5 ml der Natriumacetatlösung und 25 ml Wasser wird als Leerlösung ebenfalls in einem bedecktes Becherglas in den Exsikkator gebracht. Nach 1 stündigem Evakuieren mit der Wasserstrahlpumpe werden die Lösungen in 50-ml Messkolben transferiert, mit dest. Wasser aufgefüllt, umgeschüttelt, mit Leitungswasser auf eine konstante Temperatur gebracht und schliesslich die Messung ausgeführt. Die Eichkurve ist die gleiche wie für (*a*) (s. Fig. 3).

ZUSAMMENFASSUNG

Es wird eine Methode zur spektrophotometrischen Bestimmung von Niob unter Verwendung von Ascorbinsäure als photometrisches Reagens beschrieben. Diese bildet mit Niob einen gelbgefärbten Komplex der bei der Wellenlänge von 345 mμ maximale Extinktion aufweist. Das Gültigkeitsbereich des Beerschen Gesetzes ist sehr gross, wodurch es möglich ist, sehr geringe wie auch relativ grosse Mengen an Niob quantitativ zu erfassen.

SUMMARY

A method is described for the spectrophotometric determination of niobium, with ascorbic acid as reagent. A yellow colour is formed with an extinction maximum at 345 mμ.

RÉSUMÉ

Une méthode est décrite pour le dosage spectrophotométrique du niobium, au moyen de l'acide ascorbique comme réactif. Il y a formation d'une coloration jaune, avec extinction maximum à 345 mμ.

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APPLICATION DE LA CHRONO-AMPÉROMÉTRIE PAR REDISSOLUTION ANODIQUE AU DOSAGE DE TRACES D'ACÉTATE DE TRIPHÉNYL-ÉTAIN

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INTRODUCTION

Parmi les nombreux dérivés organiques de l'étain, étudiés par VAN DER KERK et ses collaborateurs[1], plusieurs ont été reconnus comme présentant des propriétés fongistatiques[2]; seul cependant, jusqu'à présent, l'acétate de triphényl-étain semble posséder des propriétés intéressantes qui le rendent propre à un usage agricole[3].

Aussi ne parait-il pas inutile de pouvoir mettre au point une méthode simple, rapide et suffisamment sensible, pour déterminer ce composé à l'état de traces sur végétaux ayant subi un traitement fongicide.

PRELIMINAIRES

Le dosage de faibles quantités d'acétate de triphényl-étain a été réalisé récemment par polarographie classique en mettant à profit la vague de réduction $Sn^{+2} \rightarrow Sn^{+4}$; la limite de sensibilité obtenue se situe à 6 μg dans 5 ml de liqueur (1.25 μg/ml).

Cette limite peut être considérablement améliorée en remplaçant l'électrode gouttante habituelle par une électrode à gouttes de mercure stationnaire (Electrode à goutte de mercure pendante) dont il existe à l'heure actuelle plusieurs types[5-8].

Outre les renseignements qu'il peut fournir sur le mécanisme des réactions électrochimiques[9], ce type d'électrode peut, dans un but analytique, servir de siège au dépôt pré-électrolytique des métaux amalgamables. A la fin du temps de pré-électrolyse, choisi d'autant plus long que la concentration des ions à réduire est plus faible, le potentiel, maintenu jusqu'alors à une valeur correspondant au courant limite de diffusion, est ramené, à vitesse constante, vers les valeurs plus positives. La courbe de dissolution anodique (Désalmagamation) est enregistrée au moyen de l'appareil polarographique ordinaire.

CONDITIONS OPÉRATOIRES

Appareillage

Le polarographe utilisé est du type Polarecord E 261 de Metrohm (Hérisau-Suisse).

La cellule d'électrolyse, d'une capacité de 20 ml est thermostatisée à 25° $\pm$ 0.05°. La désoxygénation des solutions est réalisée par barbotage d'azote très pur pendant 5 min.

L'électrode à goutte pendante utilisée a été conçue par VOGEL[8]; elle permet la formation aisée de gouttes de mercure reproductibles à $\pm 1\%$. La vitesse de balayage des potentiels est fixée à 333 mV/min; l'électrode de référence utilisée est du type Ag/AgCl/KCl saturé.

Les caractéristiques de la goutte étaient dans nos essais:

masse	1.32 mg	surface	4.75 mm^2
volume	0.975 mm^3	diamètre	1.23 mm

Les solutions n'ont pas été agitées au cours de la pré-électrolyse; l'atténuation (Damping) restait à la valeur nulle et le courant capacitif, très faible, n'était pas compensé.

Préparatifs analytiques

L'extraction de l'acétate de triphényl-étain sur matériel végétal est effectuée d'après les indications de GORBACH ET BOCK[4]; l'extrait chloroformique obtenu est agité dans une boule à décantation pendant 2 min avec 20 ml d'hydroxyde de potassium $N/10$ et 10 ml de tartrate dipotassique $N/2$.

Après repos, la couche chloroformique est soutirée: on rince la couche aqueuse avec 20 ml de chloroforme qu'on ajoute à la couche soutirée. On filtre les extraits chloroformiques: le filtrat, additionné de 3 ml d'acide sulfurique concentré, est évaporé au bain-marie. Le résidu d'évaporation est repris par 3 ml d'alcool et transvasé dans un vase de Berlin de 100 ml (forme haute); il y subit une minéralisation par chauffage avec le mélange habituel H_2SO_4–HNO_3 auquel, en fin d'opération, on ajoute quelques gouttes d'eau oxygénée à 100 volumes.

Le résidu minéralisé doit être incolore et exempt d'acide sulfurique qui trouble les mesures polarographiques: on chasse les dernières traces d'acide sulfurique par chauffage au four électrique à 250°.

Les produits de minéralisation sont alors dissous dans l'acide chlorhydrique 5 N; on porte à un volume connu (avec HCl 5 N) et on passe la liqueur au polarographe.

Enregistrement polarographique

La solution stannique (ou stanneuse) à analyser est introduite dans la cellule d'électrolyse et désoxygénée à l'azote très pur, pendant 5 min; puis elle est soumise à l'électrolyse sur goutte pendante de mercure à la tension de —0.7 V S.Ag.E. pendant exactement 5 min: on enregistre immédiatement le pic de dissolution anodique de l'étain entre —0.7 et —0.1 V S.Ag.E. et on se reporte à une courbe de calibrage.

Établissement de la courbe de calibrage

On prépare une solution titrée d'acétate de triphényl-étain: dans ce but, on minéralise un poids connu d'acétate de triphényl-étain dans l'acide chlorhydrique concentré; on porte à un volume connu, tel que la concentration finale en acide chlorhydrique soit 5 N. On peut encore préparer une solution titrée à partir d'étain métallique pur dissous dans l'acide chlorhydrique concentré tiède.

Dans une série de ballons jaugés de 25 ml on introduit successivement des volumes croissants de liqueur titrée en étain et on porte le volume des ballons au trait avec l'acide chlorhydrique 5 N. Après homogénéisation, on verse une partie de la solution

dans la cellule d'électrolyse en vue de l'enregistrement polarographique qu'on conduit de la manière décrite au paragraphe précédent.

La Fig. 1 représente les caractéristiques de la courbe de désamalgamation obtenue à partir d'une liqueur stanneuse contenant 0.8 μg de Sn par ml dans les conditions opératoires citées plus haut.

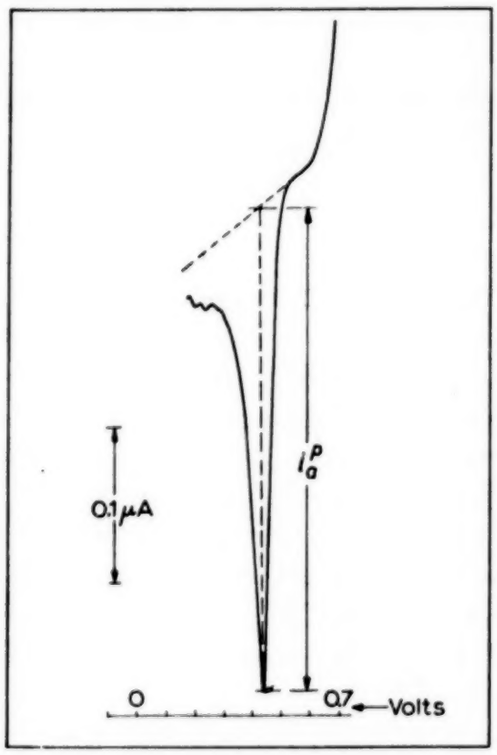

Fig. 1.

Le Tableau I rassemble les valeurs des courants de pics de dissolution obtenus dans un essai conduit en fonction de la concentration en acétate de triphényl-étain; le courant résiduel a été préalablement soustrait des valeurs mesurées.

TABLEAU I

Concentrations μg/25 ml[a]	i_a^p μA	$i_a^p/c \cdot 10^3$	*Écart %* *sur la moyenne*	
20	0.075	3.75	5.04	
40	0.138	3.45	3.36	
60	0.212	3.53	1.12	
80	0.288	3.60	0.84	
100	0.354	3.54	0.84	M = 3.57

[a] L'acétate de triphényl-étain contient 29% d'étain métal.

La précision est supérieure à celle de la polarographie classique utilisée dans le domaine des faibles concentrations.

En prolongeant le temps de pré-électrolyse et en agitant les solutions on peut observer que la limite de sensibilité est abaissée vers 0.2 μg/25 ml en acétate de tri-

phényl-étain, soit 150 fois moins que la limite qu'on obtient suivant GORBACH ET BOCK[4]. Cet accroissement considérable de sensibilité souligne l'intérêt exceptionnel de l'électrode à goutte pendante de mercure.

RÉSUMÉ

Par utilisation d'une électrode à goutte pendante de mercure (suivant VOGEL), les auteurs observent une considérable amélioration de sensibilité dans le dosage de traces résiduaires d'acétate de triphényl-étain, fongicide utilisé sur matériel végétal.

SUMMARY

Using a hanging dropping mercury electrode (according to VOGEL) the authors find a better sensitivity of measurements in the determination of triphenyl tin acetate as fungicide residues on vegetable matter.

ZUSAMMENFASSUNG

Bei der polarographischen Bestimmung von Triphenylzinn-acetat (Schädlingsbekämpfungsmittel) in Pflanzenmaterial erreicht man eine höhere Empfindlichkeit der Messungen durch Anwendung einer hängenden Quecksilbertropfelektrode.

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AMPEROMETRIC ARGENTIMETRIC AND MERCURIMETRIC TITRATION OF SULFHYDRYL

II. MERCURIMETRIC TITRATION

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In Part I of this investigation[1] data were presented on the high results obtained in the argentimetric amperometric titration of some sulfhydryl compounds containing active groups like carboxyl and amino which are responsible for extra binding of silver by silver mercaptides. The errors were found to be considerably decreased in the presence of a large excess of sulfite. For example, with thioglycolic acid the error was eliminated in the presence of 0.1 *M* sulfite. Use of this was made in the argentimetric titration of the disulfide of thioglycolic acid.

Sulfhydryl groups form mercaptides with mercury(II) which are much more stable than the corresponding silver mercaptides, and the mercury mercaptides are considerably less dissociated than the corresponding silver compounds[2]. Several sulfhydryl compounds have been titrated at the rotated platinum wire electrode (RPtWE) with mercuric chloride or acetate[3]. In addition to the formation of normal mercaptides $(XS)_2Hg$ end-points have been obtained corresponding to $(XS)_2Hg_2$ with thiol compounds containing reactive groups. The simple mercurimetric titration method could not be applied to the determination of disulfides in the presence of an excess of sulfite because the sulfite shifts the reduction of excess of mercury(II) (present as sulfito complex) at the RPtWE to such negative potentials that the mercury mercaptide is reduced before the excess of reagent. Thus it is impossible to detect an end-point at the RPtWE. On the other hand, at the dropping mercury electrode (DME) the sulfito complex of mercury(II) is reduced at potentials considerably more positive than the mercury mercaptides are and the end-point is easily detected[4]. The DME has a much smaller sensitivity than the RPtWE and is not as simple to work with as the latter. As a simple substitute for the DME it has been proposed[5] to use a rotated mercury pool electrode (RMPE) which appears to be very suitable for the amperometric mercurimetric titration of sulfhydryl and of disulfide groups in bovine serum albumin[5]. In our present studies it appeared that, contrary to the behavior at the DME, sulfite shifts the excess mercury wave at the RMPE to such negative potentials that at pH greater than 7 low molecular weight mercury mercaptides became reduced before the excess of mercury and no amperometric end-point could be determined. Apparently, a film is formed with time of standing on the surface of the electrode (RMPE, RPtWE) in solutions containing mercury(II) and sulfite and this film interferes with the reduction of the sulfito complex. No such film is formed at the DME because of the continuous formation of a fresh mercury surface.

In the present paper we have investigated the conditions under which some low molecular weight thiol compounds can be titrated accurately with mercury(II) by the amperometric technique using the RMPE as indicator electrode, and the results have been compared with those obtained at the RPtWE.

In connection with an extensive study of the equilibrium constant of the reaction of a disulfide XSSX with sulfite at varying pH

$$XSSX + SO_3^{-2} = XSSO_3^- + XS^- \qquad (1)$$

it was necessary to titrate the sulfhydryl (XS^-) formed at pH 2 where the rate of the backward reaction is negligibly small. It is shown in this paper that under specified conditions the amperometric mercurimetric titration of sulfhydryl can be carried out accurately at pH 2 at the RMPE, even when the total sulfur dioxide concentration is 10^{-2} *M*. We have applied the method to the above equilibrium studies, the results of which will be reported elsewhere. The titration at pH 2 can also be made use of in a simple determination of disulfides (*vide infra*).

EXPERIMENTAL

Materials used

Mercuric nitrate, $Hg(NO_3)_2 \cdot H_2O$, was a Baker A.R. product. Stock solutions were standardized against pure potassium thiocyanate. Mercuric chloride was a Merck reagent grade product. Other materials and experimental methods have been described in Part I[1].

The RMPE described by KOLTHOFF *et al.*[5] was used. In general an uncoated RPtWE was used. Titrations of glutathione were also carried out with a mercury-coated electrode.

RESULTS

Cysteine (RSH)

At RPtWE

Results of titrations of very dilute cysteine solutions which were 0.05 *M* in borax and 0.1 *M* in KCl (pH 9.15) are shown in Table I. Only one end-point was obtained corresponding to the formation of a compound in which cysteine and mercury are present in a molar ratio 1 : 1. Accuracy and precision were within one percent and

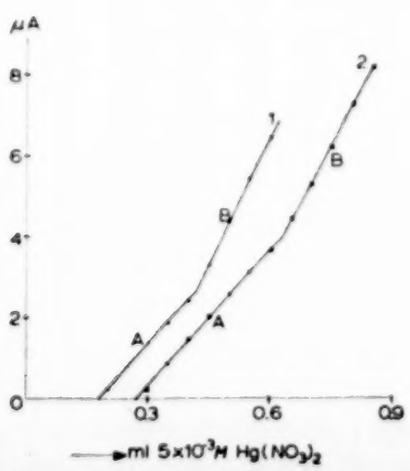


Fig. 1. Titration of cysteine with $Hg(NO_3)_2$ at RPtWE in acetate buffer pH 5.1, $E_{applied}$ = —0.2 V; (1) $4 \cdot 10^{-5}$ *M* RSH; (2) $6 \cdot 10^{-5}$ *M* RSH.

TABLE I

TITRATION OF CYSTEINE (RSH) WITH MERCURY(II) AT CLEAN RPtWE

Molarity	*Buffer*	*pH*	*Addition of chloride*	E_{appl} *vs. SCE*	*Reagent*	*Molarity of reagent*	*Molar ratio RSH to Hg at end-point*	*RSH taken mg*	*RSH found mg*	*Error %*
$3.3\cdot10^{-5}$	0.05 *M* borax	9.1	0.1 *M* KCl	—0.2	$HgCl_2$	$2\cdot10^{-3}$	1 : 1	0.1211	0.122	—1.0
$5\cdot10^{-5}$	0.05 *M* borax	9.1	0.1 *M* KCl	—0.2	$HgCl_2$	$2\cdot10^{-3}$	1 : 1	0.182	0.184	—1.3
$6.7\cdot10^{-5}$	0.05 *M* borax	9.1	0.1 *M* KCl	—0.2	$HgCl_2$	$2\cdot10^{-3}$	1 : 1	0.242	0.241	—0.5
$4\cdot10^{-5}$	0.1 *M* CH_3COONa–0.1 *M* CH_3COOH	5.1	—	—0.2	$Hg(NO_3)_2$	$5\cdot10^{-3}$	1 : 1	0.242	0.249	+2.5
$6\cdot10^{-5}$	0.1 *M* CH_3COONa–0.1 *M* CH_3COOH	5.1	—	—0.2	$Hg(NO_3)_2$	$5\cdot10^{-3}$	1 : 1	0.364	0.376	+3.3
10^{-4}	0.1 *M* CH_3COONa–0.1 *M* CH_3COOH	5.1	—	—0.2	$Hg(NO_3)_2$	10^{-2}	1 : 1	0.606	0.617	+2.0
$9.6\cdot10^{-5}$	0.01 *M* HNO_3	2.2	—	0.0	$Hg(NO_3)_2$	$5\cdot10^{-3}$	2 : 1	0.578	0.564	—2.5
$1.4\cdot10^{-4}$	0.01 *M* HNO_3	2.2	—	0.0	$Hg(NO_3)_2$	$5\cdot10^{-3}$	2 : 1	0.867	0.852	—1.5
$1.9\cdot10^{-4}$	0.01 *M* HNO_3	2.2	—	0.0	$Hg(NO_3)_2$	$5\cdot10^{-3}$	2 : 1	1.156	1.125	—2.5
$2.9\cdot10^{-4}$	0.01 *M* HNO_3	2.2	—	0.0	$Hg(NO_3)_2$	$5\cdot10^{-3}$	2 : 1	1.74	1.70	—2.3
10^{-4}	0.01 *M* HCl	2.2	—	0.0	$HgCl_2$	$5\cdot10^{-3}$	2 : 1	0.606	0.597	—1.5
$2\cdot10^{-4}$	0.01 *M* HCl	2.2	—	0.0	$HgCl_2$	$5\cdot10^{-3}$	2 : 1	1.212	1.212	0.0
$3\cdot10^{-4}$	0.01 *M* HCl	2.2	—	0.0	$HgCl_2$	$5\cdot10^{-3}$	2 : 1	1.818	1.791	—1.5

of the same order of magnitude as those reported in a previous paper[3]. Titrations of cysteine with mercuric nitrate in an acetate buffer (pH 5.1) yielded two end-points corresponding to the formation of the mercaptides $(RS)_2Hg$ and $(RS)_2Hg_2$. The results reported in Table I refer to the second end-point which is taken as the point of intersection of lines A and B in Fig. 1. At pH 5 the error was $+2.5 \pm 0.5\%$.

Similar results (-0.7 to $+2.6\%$) were reported previously[3]. The first end-point cannot be determined accurately.

Titration results of cysteine with mercuric nitrate in a medium of 0.01 *N* nitric acid at a potential of 0.0 V are also presented in Table I. At this low pH the end-point corresponds to the formation of the compound $(RS)_2Hg$. Current–potential curves of mixtures of cysteine and mercuric nitrate in 0.01 *N* nitric acid are illustrated in Fig. 2.

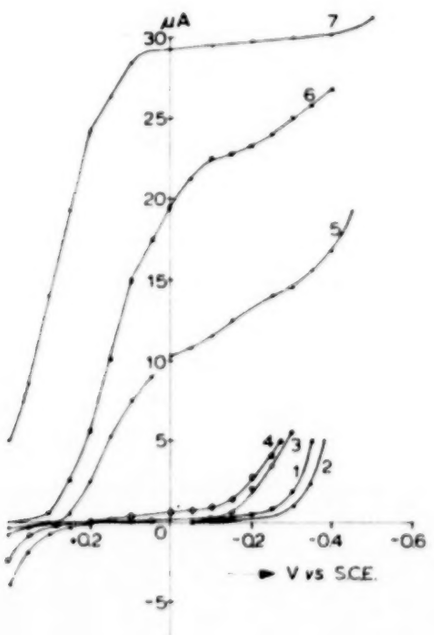


Fig. 2. Voltammograms in 0.01 *M* HNO_3 and $1.91 \cdot 10^{-4}$ *M* RSH at RPtWE. (1) 0.01 *M* HNO_3; (2) $1.91 \cdot 10^{-4}$ *M* RSH; (3) $1.91 \cdot 10^{-4}$ *M* RSH + $4.8 \cdot 10^{-5}$ *M* $Hg(NO_3)_2$; (4) + $9.55 \cdot 10^{-5}$ *M* Hg(II); (5) + $1.43 \cdot 10^{-4}$ *M* Hg(II); (6) + $1.91 \cdot 10^{-4}$ *M* Hg(II); (7) no RSH, $0.96 \cdot 10^{-4}$ *M* Hg(II).

Cysteine alone does not affect the residual current before the hydrogen reduction starts (curves 1 and 2 in Fig. 2). A reduction wave of $(RS)_2Hg$ is observed to start at about -0.15 V. When mercury is present in excess over $(RS)_2Hg$ some of the reagent is bound loosely to $(RS)_2Hg$ and the reduction wave of this excess of mercury starts at a more negative potential (about $+0.2$ V, see curves 5 and 6) as compared to that of "free" mercuric nitrate alone (curve 7), which starts at $+0.45$ V. The diffusion current of the "free" mercury (curve 7) is about 1.5 times greater than the limiting current of an excess of mercury of the same concentration. This limiting current of the excess of mercury is not well defined. A straight "excess reagent line" was found when the titration was carried out at a potential of 0.00 V (*vs.* SCE). The accuracy was $-2 \pm 0.5\%$ (Table I).

Current–potential curves were also determined in 0.01 *N* hydrochloric acid instead of nitric acid. The relations were found very much the same as in Fig. 2, except that the reduction wave of "free" mercuric chloride starts at $+0.25$ V instead of at $+0.45$V

TABLE II

TITRATION OF CYSTEINE (RSH) WITH MERCURY(II) AT RMPE

$(RS)_2Hg$ at end-point

Molarity of RSH	*Buffer*	*pH*	*Addition of chloride*	E_{app} *vs. SCE*	*Reagent*	*Molarity of reagent*	*RSH taken mg*	*RSH found mg*	*Error %*
10^{-4}	0.05 *M* borax	9.1	0.5 *M* KCl	—0.25	$HgCl_2$	10^{-2}	0.606	0.593	—2.0
$2\cdot10^{-4}$	0.05 *M* borax	9.1	0.5 *M* KCl	—0.25	$HgCl_2$	10^{-2}	1.211	1.188	—2.0
$3\cdot10^{-4}$	0.05 *M* borax	9.1	0.5 *M* KCl	—0.25	$HgCl_2$	10^{-2}	1.817	1.795	—1.2
$4\cdot10^{-4}$	0.05 *M* borax	9.1	0.5 *M* KCl	—0.25	$HgCl_2$	10^{-2}	2.423	2.375	—2.0
10^{-4}	0.1 *M* NH_4NO_3–0.04 *M* NH_3	9.0	—	—0.25	$Hg(NO_3)_2$ or $HgCl_2$	10^{-2}	0.606	0.594	—2.0
$2\cdot10^{-4}$	0.1 *M* NH_4NO_3–0.04 *M* NH_3	9.0	—	—0.25	$Hg(NO_3)_2$ or $HgCl_2$	10^{-2}	1.211	1.220	+0.6
$4\cdot10^{-4}$	0.1 *M* NH_4NO_3–0.04 *M* NH_3	9.0	—	—0.25	$Hg(NO_3)_2$ or $HgCl_2$	10^{-2}	2.423	2.447	+1.0
$6\cdot10^{-4}$	0.1 *M* NH_4NO_3–0.04 *M* NH_3	9.0	—	—0.25	$Hg(NO_3)_2$ or $HgCl_2$	10^{-2}	3.634	3.58	—1.3
10^{-4}	0.04 *M* phosphate	7.0	0.4 *M* KCl	—0.2	$HgCl_2$	10^{-2}	0.606	0.593	—2.0
$2\cdot10^{-4}$	0.04 *M* phosphate	7.0	0.4 *M* KCl	—0.2	$HgCl_2$	10^{-2}	1.211	1.182	—2.4
$4\cdot10^{-4}$	0.04 *M* phosphate	7.0	0.4 *M* KCl	—0.2	$HgCl_2$	10^{-2}	2.423	2.39	—1.0
$6\cdot10^{-4}$	0.04 *M* phosphate	7.0	0.4 *M* KCl	—0.2	$HgCl_2$	10^{-2}	3.634	3.634	0.0
$1.15\cdot10^{-4}$	0.01 *M* HNO_3	2.2	—	+0.25	$Hg(NO_3)_2$	$5\cdot10^{-3}$	0.695	0.703	+1.1
$1.5\cdot10^{-4}$	0.01 *M* HNO_3	2.2	—	+0.25	$Hg(NO_3)_2$	$5\cdot10^{-3}$	0.926	0.920	—0.6
$1.9\cdot10^{-4}$	0.01 *M* HNO_3	2.2	—	+0.25	$Hg(NO_3)_2$	$5\cdot10^{-3}$	1.157	1.15	—0.5
$3.8\cdot10^{-4}$	0.01 *M* HNO_3	2.2	—	+0.25	$Hg(NO_3)_2$	10^{-2}	2.315	2.325	+0.5
10^{-4}	0.01 *M* HCl	2.2	—	+0.05	$Hg(NO_3)_2$	10^{-2}	0.606	0.606	0.0
$2\cdot10^{-4}$	0.01 *M* HCl	2.2	—	+0.05	$Hg(NO_3)_2$	10^{-2}	1.211	1.223	+1.0
$6\cdot10^{-4}$	0.01 *M* HCl	2.2	—	+0.05	$Hg(NO_3)_2$	$2.5\cdot10^{-2}$	2.423	2.40	—0.9
10^{-3}	0.01 *M* HCl	2.2	—	+0.05	$Hg(NO_3)_2$	$2.5\cdot10^{-2}$	6.06	6.06	0.0

for mercuric nitrate. Titrations in 0.01 *N* hydrochloric acid could be carried out successfully with mercuric chloride as reagent at an applied potential of 0.0 V(see Table I).

At RMPE

Only one end-point was obtained corresponding to the formation of $(RS)_2Hg$ in mercurimetric titrations of cysteine at the RMPE under the conditions studied. Before the end-point anodic cysteine currents are observed at the RMPE at pH between 9 and 2 while no anodic currents occur at the RPtWE.

In the amperometric titrations at the RMPE the end-point was always taken as the point of intersection of the excess reagent line with the "base" line which is a horizontal line, the ordinate of which is equal to the residual current of the supporting electrolyte. In practically all cases this residual current was equal to 0 to 0.1 μA and usually could be neglected. The above method of end-point determination is preferred over the determination of the point of intersection between the anodic (XSH) current line before the end-point and the excess reagent line because the anodic current line often is not straight, the deviation being caused by film formation (*vide infra*, see also Fig. 7).

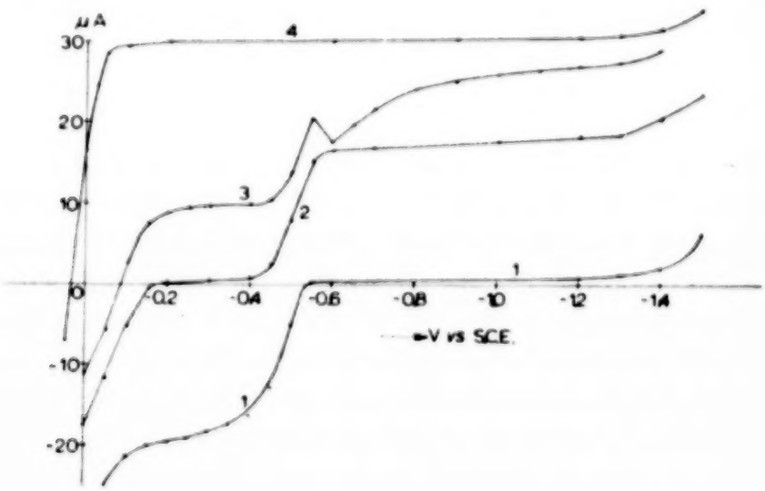


Fig. 3. Voltammograms in 0.1 *M* NH_4NO_3, 0.1 *M* NH_3 at RMPE. (1) $2 \cdot 10^{-4}$ *M* RSH; (2) $2 \cdot 10^{-4}$ *M* RSH + 10^{-4} *M* $Hg(NO_3)_2$; (3) + $1.4 \cdot 10^{-4}$ *M* $Hg(NO_3)_2$; (4) no RSH, 10^{-4} *M* $Hg(NO_3)_2$.

The current potential curves in Fig. 3 were measured at pH 9. Free cysteine gives an anodic wave with a clearly defined diffusion current which is proportional to its concentration (curve 1). When mercury(II) and cysteine are present in a molar ratio 1:2, the anodic wave of cysteine has disappeared and only the mercaptide reduction wave is observed (curve 2). On further addition of mercury(II) the excess mercury(II) wave is observed which starts at a potential about 0.1 V more negative than that observed for the free mercury ammine ions (curves 3 and 4). In the presence of excess of mercury the mercuric cysteinate wave starts to exhibit irregularities (curve 3). At a potential of —0.25 V the excess reagent line yields a straight line and the titration can be carried out successfully with mercuric nitrate or chloride (see Table II). Excess chloride does not interfere.

Equally good results were obtained in a borax buffer (pH 9) or phosphate buffer (pH 7) even at chloride concentrations as great as 0.5 *M* (Table II).

Current–potential curves in 0.01 *M* nitric acid are presented in Fig. 4. The free mercaptan wave (curve 1) and the mercaptide wave (curve 2) are shifted about 0.4 V to more positive potentials as compared to the potentials observed at pH 9. This pH effect was expected. The mercaptide wave decreases in height when there is mercury in excess over $(RS)_2Hg$ in the solution (compare curves 3 and 4 in Fig. 4). This,

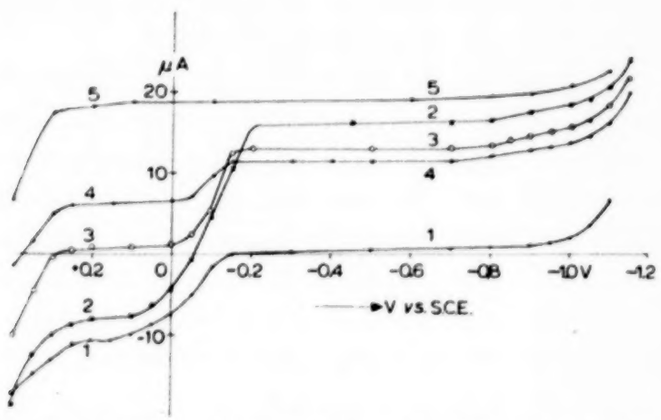


Fig. 4. Voltammograms with RSH in 0.01 *M* HNO_3 at RMPE. (1) $1.9 \cdot 10^{-4}$ *M* RSH; (2) 10^{-4} *M* $Hg(NO_3)_2$ + $2.86 \cdot 10^{-4}$ *M* RSH; (3) + $1.9 \cdot 10^{-4}$ *M* RSH; (4) + $0.95 \cdot 10^{-4}$ *M* RSH; (5) no RSH, 10^{-4} *M* $Hg(NO_3)_2$.

combined with the fact that the "excess" mercury waves start at +0.38 V as compared to +0.42 V for free mercury (curve 5) and that the limiting current of the excess mercury is smaller than that of an equal concentration of free mercury, gives strong indication of reaction to occur between $(RS)_2Hg$ and Hg(II). The excess of mercury yields a straight line at an applied potential of +0.25 V and good results are obtained in the amperometric titration at this potential (see Table II).

Current–potential curves were also run at pH 2 in the presence of varying concentrations of chloride. From these it was concluded that good results could be obtained in titrations in 0.01 *M* chloride at pH 2 at an applied potential of +0.05 V. This was confirmed by actual experiments which are reported in Table II.

Reduced glutathione (GSH)

At RPtWE

Titrations of glutathione were carried out in borax buffer in the presence and absence of chloride. In titrations carried out using a mercury-coated electrode[3] two breaks were observed corresponding to the formation of $(RS)_2Hg$ and $(RS)_2Hg_2$. Only the second can be found with some degree of accuracy. The current observed between the two breaks is decreased in the presence of chloride. From the results in Table III it appears that the error at the second break corresponding to $(GS)_2Hg_2$ is $+4.5 \pm 0.5\%$ in the absence of chloride and $-1.5 \pm 0.5\%$ in the presence of 0.1 *M* chloride. Presence of chloride is definitely beneficial at this pH. Some titrations of glutathione in 0.05 *M* borax were also carried out using an uncoated platinum electrode. Results accurate to $-0.8 \pm 0.5\%$ were obtained in the concentration range between $6 \cdot 10^{-5}$ and $3 \cdot 10^{-4}$ *M* in GSH. Chloride in a concentration of 0.1 *M* did not affect the results. With increasing concentration of glutathione the negative error became considerable.

TABLE III

TITRATION OF GLUTATHIONE (GSH) WITH MERCURIC NITRATE IN 0.05 *M* BORAX BUFFER AT RPtWE

$E_{applied}$ = —0.2 V; $(GS)_2Hg_2$ at end-point

Molarity of GSH	*Addition of chloride*	*Molarity of reagent*	*GSH taken mg*	*GSH found mg*	*Error %*	*RPtWE*
$5 \cdot 10^{-5}$	—	10^{-2}	0.768	0.799	+ 4.0	coated
10^{-4}	—	10^{-2}	1.536	1.613	+ 5.0	coated
$2 \cdot 10^{-4}$	—	10^{-2}	3.073	3.233	+ 5.2	coated
$4 \cdot 10^{-4}$	—	10^{-2}	6.146	6.392	+ 4.0	coated
$5 \cdot 10^{-5}$	0.1 *M* KCl	10^{-2}	0.768	0.783	— 2.0	coated
10^{-4}	0.1 *M* KCl	10^{-2}	1.536	1.527	— 0.6	coated
$2 \cdot 10^{-4}$	0.1 *M* KCl	10^{-2}	3.073	3.13	— 2.0	coated
$4 \cdot 10^{-4}$	0.1 *M* KCl	10^{-2}	6.146	6.20	+ 0.5	coated
$6 \cdot 10^{-5}$	—	10^{-2}	0.921	0.921	0.0	clean
10^{-4}	—	10^{-2}	1.536	1.521	— 1.0	clean
$2 \cdot 10^{-4}$	—	10^{-2}	3.073	3.043	— 1.0	clean
$3.5 \cdot 10^{-4}$	—	$2.5 \cdot 10^{-2}$	5.376	4.812	—10.5	clean
$5 \cdot 10^{-4}$	—	$2.5 \cdot 10^{-2}$	7.68	7.26	— 5.5	clean
10^{-3}	—	$5 \cdot 10^{-2}$	15.36	13.82	—10.0	clean
$6 \cdot 10^{-5}$	0.1 *M* KCl	10^{-2}	0.921	0.921	0.0	clean
$2 \cdot 10^{-4}$	0.1 *M* KCl	10^{-2}	3.073	3.027	— 1.5	clean
$5 \cdot 10^{-4}$	0.1 *M* KCl	$5 \cdot 10^{-2}$	7.68	7.22	— 6.0	clean
$7.5 \cdot 10^{-4}$	0.1 *M* KCl	$5 \cdot 10^{-2}$	11.52	9.79	—15.0	clean

Solutions which were $3.5 \cdot 10^{-4}$, $5 \cdot 10^{-4}$ and 10^{-3} *M* in GSH were titrated with negative errors of 10.5, 5.5 and 10.0% respectively. These titrations were carried out relatively rapidly. Shortly after the end-point in the titration of 10^{-3} *M* glutathione the current continued to rise and after a few minutes the observed value became considerably greater than the current measured immediately after addition of excess of mercury. This effect is caused by coating of the electrode with $(GS)_2Hg_2$ during the titration. Titrations of $5 \cdot 10^{-4}$ and $7.5 \cdot 10^{-4}$ *M* GSH carried out in the presence of 0.1 *M* chloride yielded a negative error of 6 and 15% respectively (Table III).

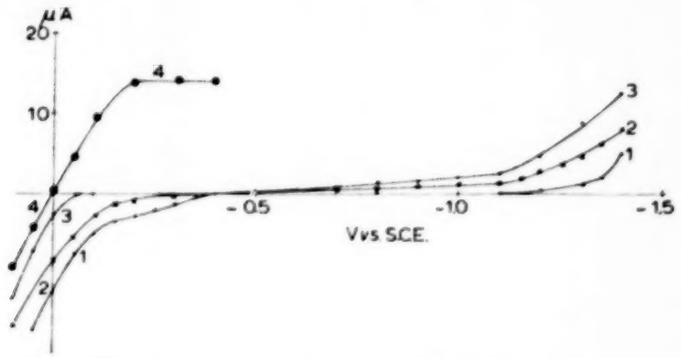
INGRAM[6] reports good results in the titration in an ammonia buffer of pH 9.2. BURTON[7] could confirm this, but also mentions an increasing positive error with increasing or decreasing pH. He reports an error of +30% both at pH of 7 and of 10.5. We have carried out titrations in ammonia buffers and did not observe a sharply defined end-point. The current at the end-point [$(GS)_2Hg_2$] was relatively large and the error fluctuated widely. Titration in borax medium in the presence of chloride is preferred at GSH concentrations of $2 \cdot 10^{-4}$ *M* or less. Quite generally, the argentimetric titration of GSH is preferred over the mercurimetric one.

Two breaks were also observed in an acetate buffer of pH 5.4 which was 0.12 *M* in sodium acetate and 0.02 *M* in acetic acid. In the titration at —0.1 V of $6 \cdot 10^{-5}$, $1 \cdot 10^{-4}$ and $2 \cdot 10^{-4}$ *M* GSH the errors were +1.0, 0.0 and —2.0% respectively. Again the end-point corresponds to a composition of $(GS)_2Hg_2$.

Titrations were also carried out in 0.01 *N* nitric acid at 0.0 V and again two breaks were observed. The second break is fairly well defined, but the current is already relatively large between the first and the second break. Using a clean electrode $4 \cdot 10^{-5}$ to $10 \cdot 10^{-5}$ *M* GSH solutions were titrated with an accuracy of ±1%.

At RMPE

Current–potential curves of GSH in mixtures with mercuric nitrate in 0.05 *M* borax solutions at the RMPE are illustrated in Fig. 5. The anodic GSH waves are clearly noticeable (curves 1 and 2) as long as the mole ratio of GSH to Hg(II) is greater than 2.



g. 5. Voltammograms of GSH in 0.05 *M* borax at RMPE. (1) $2\cdot10^{-4}$ *M* GSH; (2) $2\cdot10^{-4}$ *M* GSH + $0.5\cdot10^{-4}$ *M* $Hg(NO_3)_2$; (3) + 10^{-4} *M* $Hg(NO_3)_2$; (4) + $1.5\cdot10^{-4}$ *M* $Hg(NO_3)_2$.

However there is no diffusion plateau on the GSH waves. Peculiarly enough no reduction waves of mercury glutathionate are observed, although these are well developed at the dropping mercury electrode. The abnormal behaviour is attributed to the formation of a greyish-black film of mercury mercaptide on the surface of the mercury which interferes with the mercury mercaptide reduction but apparently not with the reduction of excess of mercuric nitrate (see curve 4 in Fig. 5). Amperometric titrations of 10^{-4} to $4\cdot10^{-4}$ *M* GSH in borax medium were carried out at a potential of —0.2 V with an accuracy of $-1 \pm 1\%$. It should be noted that the reagent line does not become straight until an excess of 25% has been added under these conditions.

The end-point is sharply defined and corresponds to a composition of $(GS)_2Hg$ and not to $(GS)_2Hg_2$ as found at the RPtWE. Apparently the loosely bound mercury, in

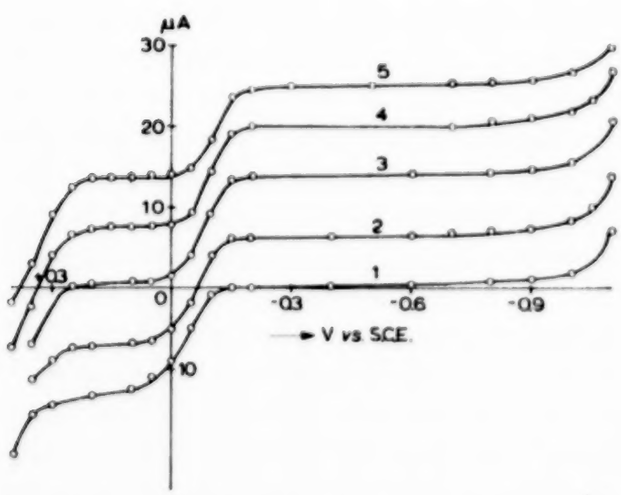


Fig. 6. Voltammograms of GSH in 0.014 *N* HNO_3. (1) 0.014 *N* HNO_3 + $2\cdot10^{-4}$ *M* GSH; (2) + $5\cdot10^{-5}$ *M* $Hg(NO_3)_2$; (3) + 10^{-4} *M* $Hg(NO_3)_2$; (4) + $1.5\cdot10^{-4}$ *M* $Hg(NO_3)_2$; (5) + $2\cdot10^{-4}$ *M* $Hg(NO_3)_2$.

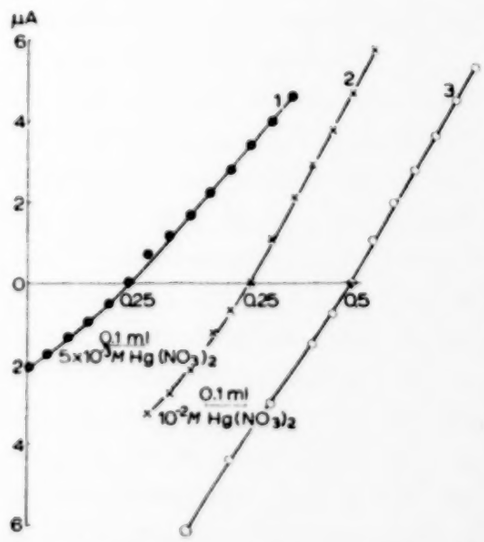


Fig. 7. Titration of GSH in 0.012 *N* HNO_3 at RMPE. $E_{applied}$ = +0.1 V. (1) $5\cdot10^{-5}$ *M* GSH; (2) $1\cdot10^{-4}$ *M* GSH; (3) $2\cdot10^{-4}$ *M* GSH.

excess over $(GS)_2Hg$, is reduced at the RMPE. From the analytical view point again, the argentimetric titration is preferred at pH 9.

In 0.014 *N* nitric acid the anodic GSH waves and the mercury glutathionate waves are well defined as illustrated in Fig. 6. The anodic GSH waves disappear when the mole ratio of GSH to Hg(II) becomes equal or smaller than 2. At a smaller ratio than 2 the excess mercury wave appears to start at potentials more positive than +0.3 V.

The amperometric titration of GSH at pH 2 and an applied potential of +0.1 V yields good results. Some examples of titration lines are given in Fig. 7. It is seen that the anodic GSH line before the end-point is not exactly a straight line. This is the reason why the end-point is taken as the point of intersection between the "base" line and the excess reagent line, as mentioned in an earlier section. In the titration of of $5 \cdot 10^{-5}$, $1 \cdot 10^{-4}$, $2 \cdot 10^{-4}$ and $4 \cdot 10^{-4}$ *M* GSH the error was 0, 0, —2, and —2.5% respectively. As is shown in a later section the titration gives excellent results at pH 2 in the presence of 0.01 *M* sulfur dioxide.

Thioglycolic acid (TSH)

At RPtWE

In the titrations of thioglycolic acid with mercuric nitrate in ammonia or borax buffers only one end-point was observed corresponding to the formation of the mercaptide $(TS)_2Hg$. Chloride did not affect the accuracy. However, in borax buffers in the presence of chloride it was necessary to wait after the end-point for two minutes before the excess mercury current became constant. This effect of chloride was not observed in ammonia buffers which are preferred as titration media. From the results in Table IV it appears that the titration yields satisfactory results.

At RMPE

Voltammograms of mixtures of thioglycolic acid and mercuric nitrate in 0.05 *M* borax solutions greatly resemble those observed with glutathione (see Fig. 5). Again,

TABLE IV

TITRATION OF THIOGLYCOLIC ACID (TSH) WITH MERCURIC NITRATE IN BORAX AND AMMONIA BUFFERS AT RPtWE

End-point $(TS)_2Hg$. $E_{applied} = -0.2$ V

Molarity of TSH	*Buffer*	*pH*	*Molarity of reagent*	*TSH taken mg*	*TSH found mg*	*Error %*
$2 \cdot 10^{-4}$	0.05 *M* borax	9.1	10^{-2}	0.921	0.939	+1.0
$5 \cdot 10^{-4}$	0.05 *M* borax	9.1	10^{-2}	2.303	2.33	+1.2
10^{-3}	0.05 *M* borax	9.1	$5 \cdot 10^{-2}$	4.606	4.66	—1.4
$2 \cdot 10^{-3}$	0.05 *M* borax	9.1	$5 \cdot 10^{-2}$	9.21	9.38	+1.8
$2 \cdot 10^{-4}$	0.05 *M* borax–0.1 *M* KCl	9.1	10^{-2}	0.921	0.921	0.0
$4 \cdot 10^{-4}$	0.05 *M* borax–0.1 *M* KCl	9.1	10^{-2}	1.84	1.89	+2.5
10^{-3}	0.05 *M* borax–0.1 *M* KCl	9.1	$5 \cdot 10^{-2}$	4.61	4.53	—1.6
$2 \cdot 10^{-4}$	0.2 *M* NH_4NO_3–0.1 *M* NH_3	9.0	10^{-2}	0.921	0.921	0.0
$4 \cdot 10^{-4}$	0.2 *M* NH_4NO_3–0.1 *M* NH_3	9.0	10^{-2}	1.84	1.88	+2.0
10^{-3}	0.2 *M* NH_4NO_3–0.1 *M* NH_3	9.0	$5 \cdot 10^{-2}$	4.61	4.57	—0.8
$2 \cdot 10^{-4}$	0.2 *M* NH_4Cl–0.1 *M* NH_3	9.0	10^{-2}	0.921	0.930	+1.0
$4 \cdot 10^{-4}$	0.2 *M* NH_4Cl–0.1 *M* NH_3	9.0	10^{-2}	1.84	1.90	+3.0
10^{-3}	0.2 *M* NH_4Cl–0.1 *M* NH_3	9.0	$5 \cdot 10^{-2}$	4.61	4.55	—1.2

film formation prevents the reduction of mercury thioglycolate, but not that of the mercury(II) in excess over $(TS)_2Hg$. A sharp end-point is observed in the titration in borax or ammonia buffers, like that at the RPtWE. Some results are given in Table V.

TABLE V

TITRATION OF THIOGLYCOLIC ACID (TSH) WITH MERCURIC NITRATE AT RMPE IN 0.05 *M* BORAX BUFFER

End-point $(TS)_2Hg$, $E_{applied} = -0.2$ V

Molarity of TSH	*Molarity of reagent*	*TSH taken mg*	*TSH found mg*	*Error %*
10^{-4}	10^{-2}	0.461	0.464	−0.8
$2 \cdot 10^{-4}$	10^{-2}	0.921	0.925	+0.4
$5 \cdot 10^{-4}$	10^{-2}	2.30	2.33	−1.0
10^{-3}	$5 \cdot 10^{-2}$	4.61	4.65	−1.0
$2 \cdot 10^{-3}$	$5 \cdot 10^{-2}$	9.21	9.28	+0.7

In 0.01 to 0.015 *N* nitric acid the voltammograms are very similar to those of GSH until the mole ratio of TSH to Hg(II) becomes smaller than 2.0. From then on the mercury mercaptide wave decreases with increasing excess of mercury and the wave exhibits maxima and shows minima and other irregularities. Also the excess of reagent wave becomes somewhat irregular. Apparently, film formation accounts for the irregularities which disappear when the solution is also 0.01 *M* in sulfur dioxide (*vide infra*). In the absence of sulfur dioxide the amperometric titration at pH 2 does not yield good results.

2-Mercaptoethanol (ESH)

At RPtWE

2-Mercaptoethanol in borax or ammonia buffers behaves towards mercury(II) at the RPtWE like thioglycolic acid and there is only one break, the end-point corresponding to $(ES)_2Hg$. As is seen from Table VI the accuracy and precision of the results are $+1 \pm 1\%$.

At RMPE

As is clear from the results in Table VII, solutions buffered with borax or ammonia can be titrated with an error of $-0.8 \pm 0.5\%$. Solutions acidified with nitric acid to pH 2 which were $4 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$ *M* in ESH were titrated with an error of −2 to

TABLE VI

TITRATION OF 2-MERCAPTOETHANOL (ESH) WITH 0.01 *M* MERCURIC NITRATE IN 0.05 *M* BORAX BUFFER AT RPtWE

End-point $(ES)_2Hg$, $E_{applied} = -0.2$ V

Molarity of ESH	*ESH taken mg*	*ESH found mg*	*Error %*
$5.1 \cdot 10^{-5}$	0.198	0.203	+2.5
$1.01 \cdot 10^{-4}$	0.396	0.398	+0.5
$2.03 \cdot 10^{-4}$	0.792	0.802	+1.3
$4.06 \cdot 10^{-4}$	1.58	1.61	+1.7
$8.1 \cdot 10^{-4}$	3.17	3.25	+2.5

+0.3%. At pH 9 as well as at pH 2 the end-point was found to correspond to the composition $(ES)_2Hg$.

TABLE VII

TITRATION OF 2-MERCAPTOETHANOL (ESH) WITH MERCURIC NITRATE AT RMPE
End-point $(ES)_2Hg$

Molarity of ESH	*Buffer*	*pH*	*E_{appl} vs. SCE*	*Molarity of reagent*	*ESH taken mg*	*ESH found mg*	*Error %*
$5 \cdot 10^{-5}$	0.05 *M* borax	9.1	—0.2	10^{-2}	0.195	0.195	0.0
10^{-4}	0.05 *M* borax	9.1	—0.2	10^{-2}	0.391	0.386	—1.3
$2 \cdot 10^{-4}$	0.05 *M* borax	9.1	—0.2	10^{-2}	0.781	0.778	—0.4
$4 \cdot 10^{-4}$	0.05 *M* borax	9.1	—0.2	10^{-2}	1.56	1.55	—0.5
$8 \cdot 10^{-4}$	0.05 *M* borax	9.1	—0.2	10^{-2}	3.13	3.11	—0.5
$4 \cdot 10^{-4}$	0.01 *M* HNO_3	2.2	+0.1	10^{-2}	1.563	1.554	—0.6
10^{-3}	0.01 *M* HNO_3	2.2	+0.1	$5 \cdot 10^{-2}$	3.91	3.83	—2.0
$2 \cdot 10^{-3}$	0.01 *M* HNO_3	2.2	+0.1	$5 \cdot 10^{-2}$	7.81	7.84	+0.3

Titration of the various thiol compounds at pH 2 in the presence of 0.01 M sulfur dioxide. Application to disulfide determination

Low molecular weight disulfides can be determined by direct amperometric titration with silver in buffers of pH 8 to 9 in the presence of sufficient sulfite[8]. However, some thiols like cysteine give a wrong end-point in this argentimetric titration[1]. The titration cannot be done mercurimetrically at pH 9 because no excess mercury line can be found. On the other hand, it was shown that the thiol titration yields good results at pH 2 in the presence of 0.01 *M* (total) sulfur dioxide at the RMPE. Results obtained with the various thiols are presented in Table VIII.

Use of this can be made in a simple determination of disulfides, which is especially advantageous when the argentimetric titration yields erroneous results. To a solution 10^{-3} *M* or more dilute in disulfide in a borax or ammonia buffer add sodium sulfite in a concentration of 0.01 *M* and enough standard mercuric nitrate or acetate to force reaction (1) quantitatively to the right. The forward reaction is very incomplete at pH 9, but it is being made complete when mercuric nitrate is added in slight excess over the amount needed to bind all XS^-. The solution is then acidified with nitric acid to pH 2 (glass electrode) and titrated with mercury(II) solution at the RMPE at +0.05 or +0.1 V.

The method was applied to the determination of cystine. The excess of mercuric nitrate added to the ammoniacal sulfite buffer was 3%. Titration results of cystine–sulfite mixtures are listed in Table IX. Solutions which were $5 \cdot 10^{-5}$ to $3 \cdot 10^{-4}$ *M* in RSSR were titrated with an error of +1%.

DISCUSSION

With the same reagent at a pH of 9 the end-point at the RPtWE is found for cysteine (RSH) and glutathione (GSH) at a mole ratio of RSH (and GSH) to mercury(II) of 1 : 1, while at the RMPE a well defined end-point is found at a mole ratio of 2 : 1. The reason for this difference in results with the two electrodes is that $(RS)_2Hg$ and $(GS)_2Hg$ bind more mercury(II), which is loosely bound[4] and which is completely reduc-

TABLE VIII

TITRATION IN 0.1 M SO_2 AT pH 2 AT RPME

End-point $(XS)_2Hg$

Molarity	*Thiol*	E_{appl} *vs. SCE*	*Molarity of* $Hg(NO_3)_2$	*Thiol taken mg*	*Thiol found mg*	*Error %*
10^{-4}	GSH	+0.1	10^{-2}	1.536	1.566	+2.0
$2\cdot10^{-4}$	GSH	+0.1	10^{-2}	3.07	3.10	—1.0
$4\cdot10^{-4}$	GSH	+0.1	10^{-2}	6.15	6.15	0.0
$6\cdot10^{-4}$	GSH	+0.1	$5\cdot10^{-2}$	9.22	9.46	—2.6
$4\cdot10^{-5}$	RSH	+0.05	10^{-2}	0.242	0.242	0.0
10^{-4}	RSH	+0.05	10^{-2}	0.605	0.605	0.0
$2\cdot10^{-4}$	RSH	+0.05	10^{-2}	1.21	1.22	+0.6
$4\cdot10^{-4}$	RSH	+0.05	10^{-2}	2.42	2.43	+0.3
$6\cdot10^{-4}$	RSH	+0.05	10^{-2}	3.63	3.61	—0.7
$8\cdot10^{-4}$	RSH	+0.05	10^{-2}	4.85	4.81	—0.8
10^{-4}	TSH	+0.05	10^{-2}	0.461	0.468	+1.6
$5\cdot10^{-4}$	TSH	+0.05	10^{-2}	2.30	2.35	+2.0
10^{-3}	TSH	+0.05	$5\cdot10^{-2}$	4.61	4.62	—0.4
$2\cdot10^{-3}$	TSH	+0.05	$5\cdot10^{-2}$	9.21	9.31	+1.0
$2\cdot10^{-4}$	ESH	+0.1	10^{-2}	0.781	0.789	+1.0
$4\cdot10^{-4}$	ESH	+0.1	10^{-2}	1.56	1.575	+1.0
$8\cdot10^{-4}$	ESH	+0.1	10^{-2}	3.13	3.17	+1.2
$1.5\cdot10^{-3}$	ESH	+0.1	$5\cdot10^{-2}$	5.86	5.90	+0.7

TABLE IX

TITRATION OF CYSTINE ACCORDING TO PROCEDURE GIVEN IN THE TEXT WITH 0.01 M MERCURIC NITRATE AT RMPE

$E_{applied} = +0.05$ V

Molarity of RSSR	*RSSR taken mg*	*RSSR found mg*	*Error %*
$5\cdot10^{-5}$	0.600	0.600	0.0
10^{-4}	1.201	1.21	+0.8
$2\cdot10^{-4}$	2.403	2.427	+1.0
$3\cdot10^{-4}$	3.604	3.64	+1.1

ed at the applied potential at the RMPE but yields only small currents at the RPtWE. A large increase in current at the platinum electrode is observed after formation of $(RS)_2Hg_2$ and $(GS)_2Hg_2$. With thioglycolic acid (TSH) and 2-ethanol mercaptan (ESH) the end-point at both electrodes at pH 9 is found at a mole ratio of 2 TSH or 2 ESH to 1 Hg(II). At the (clean) platinum electrode no anodic current of the thiol compound is observed at the applied potential, while at the RMPE an anodic current is observed before the end-point as illustrated in Fig. 7. In the first part of this study[1] it was stated that the argentimetric amperometric titration at pH 9 of cysteine and of thioglycolic acid yield large positive errors. Particularly for these two compounds the titration at the RMPE is recommended which yields excellent results over a wide range of concentrations.

The binding of more than one mercury(II) per two sulfhydryl groups occurs with RSH, GSH and TSH, but not with ESH. The first three contain other functional

groups (carboxyl, and also amino in RSH and GSH) which are responsible for further mercury binding. We are continuing the argentimetric and mercurimetric studies with several other mercaptans in order to get further insight in the role of various functional groups in the extra binding of silver and mercury by the normal mercaptides.

The disulfide determination by making the solution buffered at pH 9 with borax or ammonia 0.01 *M* in sulfite followed by adding standard mercuric nitrate solution in slight excess over $(XS)_2Hg$, acidifying with nitric acid to pH 2, and measuring the excess reagent line, is of special advantage in an assay of cystine. With this compound the direct argentimetric titration yields high results[1]. For the determination of the disulfides of GSH, TSH and ESH the direct ampero-argentimetric method is simpler and preferred.

In connection with our studies of the equilibrium constants between disulfides and sulfite at varying pH it is gratifying that the equilibrium concentration of the thiol compounds can be titrated at pH 2 with mercuric nitrate at the RMPE. This method had been applied already to the determination of disulfide in denatured bovine serum albumin[5]. Here the situation is simpler than with low molecular weight thiol compounds because the mercury mercaptides of albumin are not reduced at a RMPE.

ACKNOWLEDGEMENT

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SUMMARY

The ampero-mercurimetric titration of cysteine (RSH), glutathione (GSH), thioglycolic acid (TSH) and 2-mercaptoethanol (ESH) at the RMPE at pH 9 yields a sharply defined end-point corresponding to the composition $(XS)_2Hg$. Under the same conditions with the RPtWE two breaks are observed in the titration lines with RSH and GSH, corresponding to compositions $(RS)_2Hg$ and $(RS)_2Hg_2$ respectively. On the other hand, with TSH and ESH only one clear break is found at the RPtWE corresponding to $(TS)_2Hg$ or $(ES)_2Hg$. Conditions have been described for the accurate mercurimetric titration of the thiol compounds at pH 2 in the presence of 0.01 *M* sulfur dioxide at the RMPE. Use of this can be made in the determination of disulfides and in the determination of the equilibrium concentrations of the reaction between a disulfide and a sulfite at varying pH.

RÉSUMÉ

Les auteurs ont effectué une étude sur le titrage ampérométrique de la cystéine, de la glutathione, de l'acide thioglycolique et du mercapto-2-éthanol, par mercurimétrie. Ils ont examiné également le comportement des disulfures et la détermination des concentrations d'équilibre, à divers pH, entre disulfure et sulfite.

ZUSAMMENFASSUNG

Beschreibung einer ampero-mercurimetrischen Methode zur Bestimmung von Cystein, Glutathion, Thioglycolsäure und 2-Mercapto-äthanol. Die Methode lässt sich verwenden zur Bestimmung von Disulfiden und Gleichgewichtskonzentrationen bei der Reaktion zwischen einem Disulfid und Sulfit bei verschiedenem pH.

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SPECTROPHOTOMETRIC DETERMINATION OF ALUMINIUM WITH STILBAZO

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Stilbazo (stilbene-4,4′-bis(1-azo-3,4′-dihydroxybenzene)-2,2′-disulfonate) has been proposed as a spectrophotometric reagent for aluminium[1]. The reagent has been used for the determination of aluminium in iron and steel[2,3].

In the present work the results of an investigation of stilbazo as a spectrophotometric reagent for aluminium are presented.

EXPERIMENTAL

Apparatus and solutions

Apparatus. A Beckman Spectrophotometer, Model DU, with 1-cm cells was used for the absorption measurements. The pH was measured with a Beckman H-2 type pH-meter.

Aluminium standard solution. 1.349 g of spectrographically pure aluminium was dissolved in hydrochloric acid and the solution was diluted to 1 l with distilled water. From this standard solution more dilute solutions were prepared as required.

Reagent solution. 0.120 g of stilbazo was dissolved in 1 l of distilled water.

Buffer solution. 24 g of sodium acetate trihydrate was dissolved in 1 l of distilled water. The pH was adjusted to 5.65 by dropwise addition of concentrated acetic acid.

Procedure

An aliquot of the aluminium standard solution was pipetted into a 25-ml volumetric flask and 5 ml of the reagent solution and 10 ml of the buffer solution were added. The solution was diluted to volume with distilled water and the absorption was measured against a reagent blank.

RESULTS AND DISCUSSION

Absorption curves

The absorption of the aluminium complex against both reagent solution and distilled water and that of the reagent solution against distilled water were measured as a function of wavelength. The values are plotted in Fig. 1. The absorption curve of the aluminium complex shows a maximum at 500 mμ and all subsequent measurements were made at that wavelength.

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Effect of pH, time, temperature and reagent concentration

Solutions of the reagent and solutions containing aluminium and reagent were adjusted to various pH values with sodium acetate–acetic acid buffer solutions. In Fig. 2 the absorption of the reagent solution and the absorption of the aluminium complex are plotted as a function of pH. The absorption of the aluminium complex

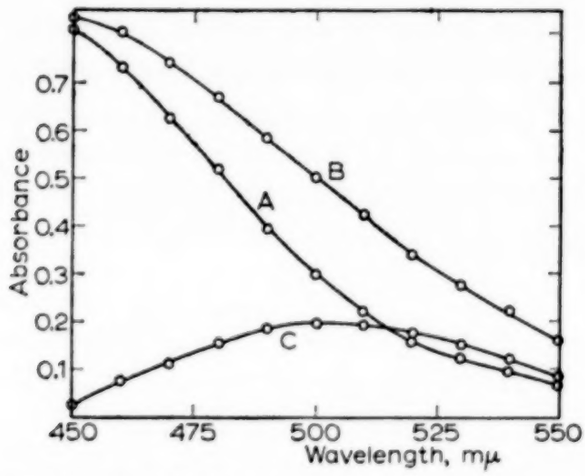

Fig. 1. Absorption spectra of reagent and its aluminium complex. A, Reagent against water; B, Reagent plus aluminium against water; C, Reagent plus aluminium against reagent.

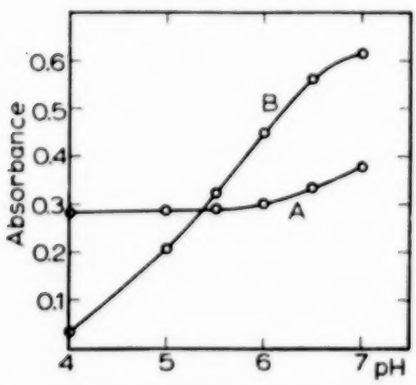

Fig. 2. A, Effect of pH on the reagent; B, Effect of pH on the complex.

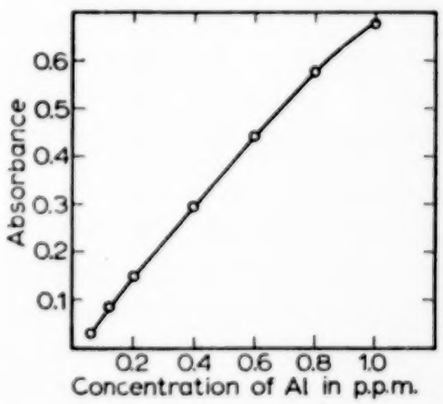

Fig. 3. Beer's law curve.

increased almost linearly in the range pH 4–7. The absorption of the reagent solution was approximately constant between pH 4 and 5.8. Above 5.8 the absorption increased.

The colour of the aluminium complex was found to be stable for at least 3 h. The colour remained unchanged under normal conditions of light and temperature (20–30°).

The absorption of the aluminium complex increased slightly with increasing reagent concentration. With sufficient excess of reagent it was, however, practically independent of the reagent concentration.

The buffer concentration did not affect the absorption of the complex up to about 0.25 g sodium acetate per 25 ml. Higher buffer concentrations caused decreasing colour intensities.

Beer's law

Different quantities of the aluminium standard solution were mixed with 10 ml of reagent and 10 ml of buffer solution. The solutions were diluted to 25 ml and their absorbancies were measured at 500 mμ against a reagent blank. Beer's law was found to be obeyed in the concentration range 0.1–0.8 p.p.m. aluminium. A slight deviation from Beer's law was found at lower and higher concentrations.

Composition, molar extinction coefficient and instability constant

The empirical formula of the coloured aluminium–stilbazo complex was determined by the method of "continuous variation" and by the "mole ratio" method. The results suggest a 1 : 1 complex of aluminium with the reagent.

The molar extinction coefficient of the complex was calculated to be 19,500. The instability constant calculated from the relationship[4]

$$K = \frac{\alpha^2 C}{1 - \alpha} \quad (\alpha = \frac{Em - Es}{Em})$$

was found to be equal to $5.96 \cdot 10^{-6}$.

Effect of foreign ions

Oxalate, tartrate, citrate, NTA, EDTA and fluoride interfered by bleaching the colour even in concentrations comparable with that of aluminium. Copper, tin(II), molybdenum(VI), tungsten(VI), titanium(IV), vanadium(IV) and (V) and iron(II)and (III) interfered by deepening the colour when present in 1:1 ratio with aluminium. Chromium(III) caused the colour to fade. Ions that could be tolerated in higher concentrations are listed in Table I.

TABLE I

TOLERANCES TO DIVERSE IONS
Aluminium concentration, 0.3 p.p.m.

Ion	*P.p.m. tolerated*	*Ion*	*P.p.m. tolerated*
Sn(IV)	30	Nb(V)	3
Co	300	As(III)	100
Ni	30	As(V)	10
Zn	30	Pb	30
Cd	30	Mn(II)	300
Ca	300	PO_4	5
Mg	300	Cl (as NaCl)	1000
Cr(VI)	4	SO_4 (as Na_2SO_4)	10000
		NO_3 (as $NaNO_3$)	1000
		NH_4 (as NH_4Cl)	1000

SUMMARY

The use of stilbazo as a spectrophotometric reagent for aluminium has been investigated. The reagent forms a stable coloured complex with aluminium showing an absorption maximum at 500 mμ. The system obeys Beer's law from 0.1–0.8 p.p.m. aluminium. The molar extinction coefficient and the stoichiometric composition of the coloured complex have been determined.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'emploi du "stilbazo" comme réactif pour le dosage spectrophotométrique de l'aluminium. Le complexe formé est stable, avec maximum d'absorption à 500 mμ.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Verwendung von "Stilbazo" als Reagens für die spektrophotometrische Bestimmung von Aluminium.

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Buchbesprechungen

Gmelins Handbuch der anorganischen Chemie, 8. Auflage, *Sauerstoff (Lieferung 4) System Nr. 3*, 1960, XV+366 Seiten, 76 Figuren, Verlag Chemie G.m.b.H. Weinheim/Bergstrasse, Kartoniert DM 223,—.

Die Lieferung 4 zum Band *Sauerstoff* umfasst die Kapitel Luft, aktiver Sauerstoff und Ozon unter Berücksichtigung der Literatur bis Ende 1949. Im Kapitel Luft sind in diesem Band lediglich die physikalischen Eigenschaften beschrieben. Das chemische Verhalten ist in den Bänden der jeweiligen Reaktionspartner zu finden.

Nach einem Überblick über die Zusammensetzung und Aggregatzustände der Luft folgt eine Beschreibung der mechanisch-thermischen, akustischen, optischen, magnetischen und elektrischen Eigenschaften unter besonderer Berücksichtigung der Zustandsgleichungen und des Joule-Thomson Effektes. Im Kapitel über aktiven (atomaren) Sauerstoff werden dessen Bildung und Darstellung, Nachleuchtspektrum und thermisches Verhalten behandelt. Der grösste Teil des Bandes befasst sich mit dem Ozon. Nach einem kurzen geschichtlichen Überblick folgt ein sehr ausführlicher Abschnitt über Bildung und Zerfall, worin zunächst die Gleichgewichte $3\ O_2 \rightleftharpoons 2\ O_3$ und $O_2 + O \rightleftharpoons O_3$ im thermischen und photochemischen Prozess sowie in elektrischen Entladungen in Sauerstoff und Luft beschrieben werden. Es folgen dann Abhandlungen über thermische und photochemische Bildung und Zerfall, über Bildung und Zerfall in elektrischen Entladungen (vor allem stille Entladung, Ozonapparate), bei Einwirkung von Ladungsträgern (Elektronen und α-Strahlen) sowie über die Bildung bei elektrolytischen und chemischen Vorgängen. Anschliessend werden die Methoden und Apparate zur Darstellung von Ozon im Laboratorium beschrieben unter Angabe der für maximale Ausbeuten erforderlichen Bedingungen (die technischen Verfahren sind bereits in der Lieferung 2 behandelt). Der Abschnitt über physikalische Eigenschaften befasst sich mit Fragen der Molekülstruktur, den mechanisch-thermischen, optischen, magnetischen und elektrischen Eigenschaften mit Daten neuerer Messungen. Im Abschnitt über das elektrochemische Verhalten werden das Normalpotential Einzelpotentiale und Ketten gegen Wasserstoff, Sauerstoff und Quecksilber behandelt.

Das Schlusskapitel des Bandes befasst sich mit dem chemischen Verhalten des Ozons im allgemeinen, gegen Nichtmetalle, Metalle, anorganischen Stoffen, wobei in einem besonderen Abschnitt die Reaktionen wässriger Ozonlösungen gegen Anionen und Kationen beschrieben werden. Der letzte Teil dieses Abschnitts behandelt dann noch einige organische Lösungsmittel für Ozon. Der Band ist mit Marginalien in englischer Sprache versehen und enthält ein deutsch–englisches Inhaltsverzeichniss.

K. EDER (Genf)

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Gmelins Handbuch der anorganischen Chemie, 8. Auflage, *Strontium* (*Ergänzungsband*) *System Nr. 29*, 1960, iv, xxx, 306 Seiten, 39 Figuren, Verlag Chemie G.m.b.H., Weinheim/Bergstrasse, Kartoniert DM 195.—, Ganzleinen DM 200.—.

Der Ergänzungsband zu dem 1931 erschienenen Band *Strontium* umfasst die Forschungsergebnisse von 1932 bis 1949. Ausser dem Element werden noch die Verbindungen des Strontiums mit den Nichtmetallen sowie mit den Metallen As, Sb, Bi, Be, Mg, Ca und Alkalimetalle behandelt. Ungefähr ein Viertel des Bandes befasst sich mit dem Vorkommen des Strontiums, wobei neben den Lagerstätten auch das Vorkommen in der Hydrosphäre und Biosphäre behandelt wird. Ferner wird auf die Bedeutung der Strontium-Isotope für die geologische Alterbestimmung hingewiesen. Das Kapitel über die Technologie des Strontiums und seiner Verbindungen beschreibt die Verfahren zur Aufbereitung und den Aufschluss der Ausgangsmaterialien, die technischen Darstellungsmethoden für das Strontiummetall und die wichtigsten Verbindungen mit Angaben über deren Verwendung. Im Kapittel über die Darstellung des Elementes werden auch die Methoden zur Anreicherung und Abtrennung der Strontium-Isotope besprochen. Ein Abschnitt über physiologische Schädigungen weist auf die Gefahren im Umgang mit Strontiumverbindungen hin. Nach der Behandlung der physikalischen Eigenschaften wird das elektrochemische und chemische Verhalten des Elementes bezw. Ions besprochen, wobei auch die analytischen Reaktionen berücksichtigt wurden. Etwa die Hälfte des Bandes befasst sich mit den Verbindungen des Strontiums. Nach den Legierungen mit Ca folgen die Verbindungen mit H, O, N, Halogen, S mit besonders ausführlicher Behandlung des Strontiumchlorids und -sulfates. Anschliessend werden die Verbindungen mit B, C, Si, P, As, Sb, Bi, Be, Mg, Ca und Alkalimetallen beschrieben. Der Band ist mit Marginalien in englischer Sprache versehen und enthält ein deutsch–englisches Sachregister.

K. EDER (Genf)

Anal. Chim. Acta, 24 (1961) 298

Polarographisches Praktikum par J. HEYROVSKÝ, Zweite neubearbeitete Auflage (Anleitungen für die chemische Laboratoriumspraxis, Band IV) vii + 116 Seiten, mit 105 Abbildungen. Springer Verlag, Berlin, 1960, 19.80 DM.

Remarquable ouvrage à double titre, d'abord parce qu'il présente en quelques 116

pages, en un exposé clair et concis, l'une des plus étonnantes méthodes d'investigation de la science moderne, d'autre part parce que celui qui l'a écrit est le créateur de la méthode, ce qui lui a valu le prix Nobel de Chimie 1959.

Ce livre est destiné à tous ceux qui désirent pratiquer la polarographie et les méthodes qui en découlent. Les explications en sont si simples et si complètes que chacun peut, sans aide extérieure appliquer cette méthode, même s'il n'a aucune connaissance du sujet.

Cet ouvrage comprend deux parties; la première traite de l'appareillage et des processus de mesure. La seconde décrit un certain nombre d'applications pratiques particulièrement bien choisies car elles permettent au néophyte de parfaire les connaissances acquises dans la première partie.

Le livre débute par une description des appareils, du plus simple qu'il est aisé de construire soi-même avec les moyens du bord — et l'auteur donne toutes précisions à ce sujet — jusqu'aux polarographes enregistreurs. Les oscillographes et les dispositifs à rayons cathodiques ne sont pas décrits, ils n'ont que faire dans un livre qui s'adresse plus particulièrement aux personnes non spécialisées. Il est aussi question d'électrode à goutte de mercure, d'électrolytes de base, de sensibilité et de précision. Les diverses cuves polarographiques macro et micro sont décrites ainsi que la technique d'essais des appareils, de la titration polarographique, etc.

Dans la seconde partie, l'auteur propose quelques applications, tant qualitatives que quantitatives; il en profite pour décrire un certain nombre de phénomènes importants en polarographie tels que: effet de l'oxygène dissous et les moyens de s'en débarrasser, les maximums et les suppresseurs de maximum; les courants cinétiques et leur interprétation. L'auteur décrit aussi quelques processus d'oxydation et de réduction organiques et inorganiques, le problème des séparations et les déterminations microanalytiques. L'ouvrage se termine par des tabelles de potentiels de dépolarisation.

Le tout est exposé en une progression régulière; à aucun moment l'auteur n'accumule les difficultés, elles viennent les unes après les autres sans hâte, aussi s'initie-t-on sans peine à cette remarquable méthode. Il m'a très rarement été donné de lire un ouvrage présentant de telles qualités didactiques.

D. MONNIER (Genève)

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Systematic Analysis of Surface-active Agents von MILTON J. ROSEN UND HENRY A. GOLDSMITH, Interscience, New York, 1960, 422 Seiten, Preis: $13.50.

In der Reihe der Monographien *Chemical Analysis* ist jetzt als Band 12 eine ausführliche Behandlung der systematischen Analyse oberflächenaktiver Substanzen erschienen. In einer kurzen Einleitung werden zunächst die verschiedenen Klassifizierungsmöglichkeiten besprochen. Da die übliche Einteilung in anionen- und kationenaktive, nicht-ionogene und ampholytische Verbindungen für die chemische Analyse dieser Substanzen unpraktisch ist, wird dem beschriebenen Analysengang eine Einteilung nach den vorhandenen Elementen zu Grunde gelegt: (*I*) enthält nur C-H-O; (*II*) enthält C-H-O + Metall; (*III*) enthält C-H-O + S; usw. Im 2. Kapitel folgen dann Angaben über Nachweisreaktionen für oberflächenaktive Substanzen

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(ohne Berücksichtigung der Zugehörigkeit zu den einzelnen Typen), über deren Abtrennung von Begleitstoffen durch Extraktion, Austauscherharze oder Chromatographie sowie quantitative Bestimmung nach Gruppen in Stoffgemischen. Das 3. Kapitel befasst sich mit der qualitativen Analyse der oberflächenaktiven Substanzen, wobei auch physikalische Methoden (IR und UV Absorption, Röntgenstrahlenbeugung) berücksichtigt sind. Die chemischen Methoden erstrecken sich auf den Nachweis der Elemente und funktionellen Gruppen. Der letzte Teil dieses Kapitels beschreibt dann Methoden zur Identifizierung einzelner oberflächenaktiven Substanzen durch Säurezahl, Jodzahl, Hydroxylzahl usw. Im 4. Kapitel werden die Methoden zur quantitativen Bestimmung beschrieben, wobei ebenfalls die Gruppierung nach Elementen als Grundlage dient. Sehr ausführlich werden dann im 5. Kapitel die Methoden zur Trennung von Gemischen oberflächen-aktiver Substanzen behandelt. Der Anhang enthält eine Liste der bekanntesten im Handel (USA) befindlichen Surfactants mit Angaben über die chemische Zusammensetzung und deren Hersteller. In einer zweiten Tabelle werden die Brechungsindices der wichtigsten Ausgangsprodukte und einer Anzahl Fertigprodukte aufgeführt. Eine dritte Tabelle gibt Daten über Titer, SZ und JZ der Fettsäuren handelsüblicher Qualität mit Angaben über Zusammensetzung und Lieferanten. Sowohl die einzelnen Kapitel wie auch die Tabellen sind durch zahlreiche Literaturreferenzen ergänzt.

Man muss den Autoren dankbar sein, dass sie es unternommen haben, die weit verstreuten Literaturangaben zu sichten und die besten Methoden in einem Buch zusammen-zu-fassen und durch eigene Vorschriften zu ergänzen. Die Anordnung ist sehr glücklich gewählt, der Text kurz aber präzis und die Analysengänge sehr übersichtlich durch die Anwendung des "Flowsheet" Prinzips. Das Buch ist vor allem für die Laboratoriumspraxis bestimmt und kann bestens empfohlen werden.

K. EDER (Genf)

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Announcement

CONGRESS FOR ANALYTICAL CHEMISTRY

A Congress on analytical chemistry will be held in Budapest, Hungary, from the 24th to 29th April, 1961, under the auspices of the Hungarian Academy of Sciences and with the patronage of the International Union of Pure and Applied Chemistry.

The Congress will deal with the following subjects: Theoretical basis of chemical analysis; analytical applications of isotopes; complex chemistry and its analytical application; organic analysis; electroanalytical methods; chromatography; spectrochemical analysis; applied analysis. Plenary lectures will be given by Professors I. P. ALIMARIN (USSR), R. BELCHER (UK), G. CHARLOT (France), C. DUVAL (France), L. ERDEY (Hungary), L. GORDON (USA), J. HEYROVSKÝ (Czechoslovakia), K. JACIMIRSZKIJ (USSR), W. KEMULA (Poland), E. SCHULEK (Hungary), S. VEIBEL (Denmark), PHIL. W. WEST (USA), W. F. K. WYNNE-JONES (UK) and W. J. KIRSTEN (Sweden).

Further information can be obtained from:

Magyar Kemikusok Egyesulete "Analitikai Kongresszus"
Budapest V, Szabadsag ter 17, Hungary.

EXTRACTION OF BISMUTH AS IODIDE WITH ISOAMYL ACETATE AND ISOAMYL ALCOHOL

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(Received September 24th, 1960)

The separation of traces of bismuth from most elements can often be carried out advantageously by dithizone extraction from basic medium, in the presence of cyanide if need be, to complex otherwise reacting heavy metals except lead, thallium and indium. This method is likely to be inapplicable in the presence of much calcium (or magnesium) and phosphate which will give a precipitate in basic medium even in the presence of citrate. We have therefore studied the extraction of bismuth as the iodide or iodobismuthous acid from strongly acid solution as a means of isolating bismuth from such samples. In some respects this extraction method is more convenient than isolation of bismuth by hydrogen sulfide precipitation and moreover is more selective. Cupferron–chloroform and diethylammonium diethyldithiocarbamate–chloroform extraction are other possible methods for the isolation of bismuth from acid medium; although a number of metals are extracted under the same conditions as bismuth, these methods may be superior to the iodide extraction for some types of samples.

Choice of solvents

Contrary to some statements in the literature, bismuth iodide and iodobismuthous acid are not extracted by non-oxygen solvents such as chloroform and benzene. An oxonium type organic solvent is required, but these vary greatly in their effectiveness. Bismuth is extractable both as BiI_3 and $HBiI_4$ (or other iodobismuthous acids), depending on the solvent and the iodide concentration. Extraction as $HBiI_4$ is likely to be disadvantageous because a relatively large number of other metals can also be extracted as iodo acids[1,2]. In general, a solvent extracting bismuth as BiI_3 will be preferred, and this type of extraction is considered here. Solvents which will effectively extract bismuth from acid solution at low iodide concentrations (approximately 0.01 *M*), where BiI_3 is the predominant bismuth–iodide species, include butyl acetate, isobutyl acetate, amyl acetate, isoamyl acetate, and isoamyl alcohol. Butyl butyrate, ethyl ether, and ethyl oxalate are less effective. Benzyl acetate, butyl propionate, amyl propionate, and ethyl benzoate dissolve only limited amounts of bismuth iodide.

Isoamyl acetate and isoamyl alcohol were selected for further study. The former especially seemed worth investigation because of its preferential extraction of bismuth iodide.

EXPERIMENTAL

Solvents

The isoamyl acetate used was a "certified reagent" product (Fisher), b.p. 129–132°, not further purified. The isoamyl alcohol was Eastman's practical grade, b.p. 138–141°; it was not purified.

General procedure

20 ml of aqueous phase, containing bismuth as sulfate ($5 \cdot 10^{-4}$ *M*), sulfuric acid and potassium iodide, was shaken at 25–30° for 10 min with 5.0 ml of organic solvent. Bismuth was determined by the spectrophotometric iodide method[3] in the phase containing the lesser concentration of bismuth. Bismuth was removed from the organic solvent phase before determination by shaking the latter with five 4-ml portions of 3 *N* sulfuric acid.

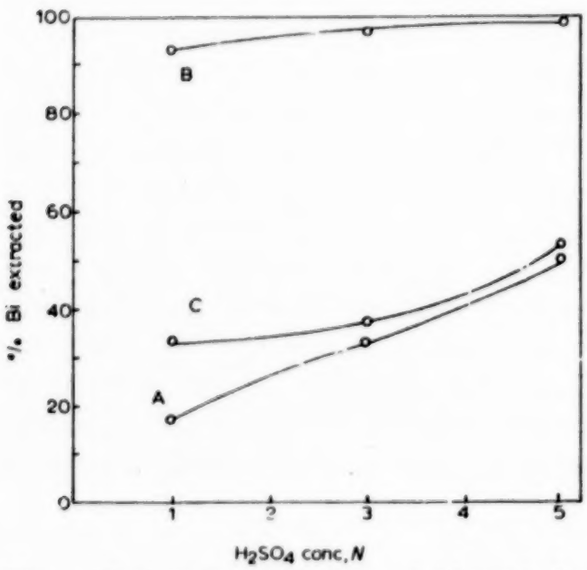

Fig. 1. Percentage extraction of bismuth by isoamyl acetate at various iodide concentrations as a function of sulfuric acid concentration. 20 ml aqueous phase ($5 \cdot 10^{-4}$ *M* Bi), 5 ml isoamyl acetate. A, 0.0010 *M* KI; B, 0.0065 *M* KI; C, 0.1000 *M* KI.

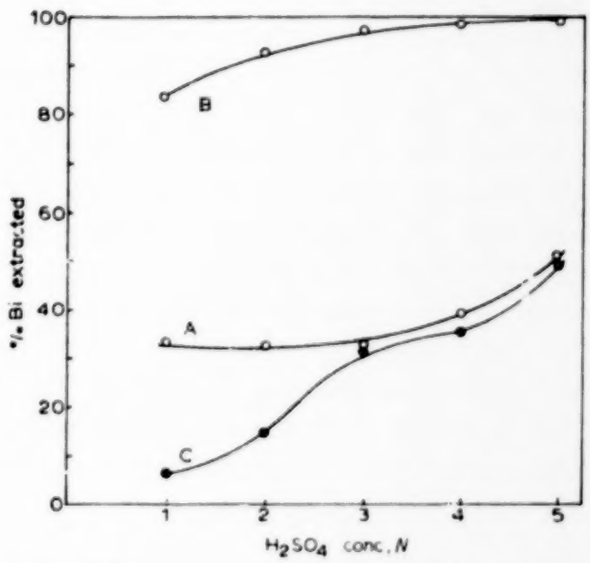

Fig. 2. Percentage extraction of bismuth by isoamyl acetate from 3.0% sodium hypophosphite solutions (conditions otherwise as in Fig. 1). A, 0.0010 *M* KI; B, 0.0065 *M* KI; C, 0.1000 *M* KI.

Factors affecting extraction of bismuth as iodide

Of chief interest are the effects of acidity, iodide concentration and bismuth concentration. Since in practical work the presence of oxidizing agents, such as ferric iron, must be expected, most of the extractions were carried out in the presence of a reducing agent, usually sodium hypophosphite. In Fig. 1 the extractability of bismuth with isoamyl acetate as a function of the sulfuric acid concentration at three different iodide concentrations is shown. Fig. 2 represents the same system except that the aqueous solution contained sodium hypophosphite (3.0% or approximately 0.3 *M*). The decrease in extractability produced by hypophosphite is probably to be attributed to the complexing of bismuth. At high acidity (>3.5 *N* H_2SO_4) and the most favorable iodide concentration (approximately 0.0065 *M* I^- total), hypophosphite has little effect as might be expected, since the ionization constant of hypophosphorous

acid is about 0.01 and most of it is present in the undissociated form in strongly acid solution.

Table I contains data for comparison of the extractability of bismuth by isoamyl acetate from sulfuric and perchloric solutions of the same normality, each 0.0065 *M*

TABLE I

EFFECT OF ACIDITY ON EXTRACTION OF BISMUTH

20 ml of aqueous phase 0.0065 *M* in potassium iodide, $5 \cdot 10^{-4}$ *M* in Bi and 3.0% in sodium hypophosphite; 5 ml isoamyl acetate

Acid concentration *N*	% *extraction* H_2SO_4	$HClO_4$
1.0	83.7	94.2
2.0	92.5	97.2
3.0	97.0	99.2
5.0	98.9	—

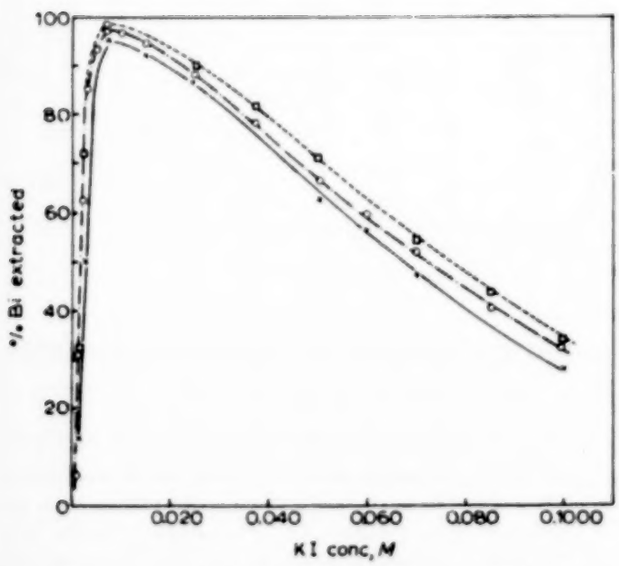

Fig. 3. Percentage extraction of bismuth by isoamyl acetate as a function of iodide concentration in presence of sodium hypophosphite and ascorbic acid (0.05%)–sodium sulfite (0.01%). Sulfuric acid concentration (original) 3.0 *N* in each. 20 ml aqueous phase, 5 ml isoamyl acetate. □, ascorbic acid–sulfite; ○, 3% sodium hypophosphite, ×, 6% sodium hypophosphite.

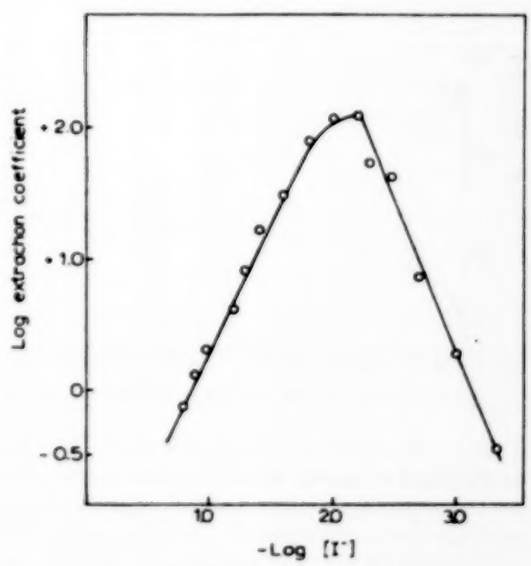

Fig. 4. Logarithmic plot of extraction coefficient ($[Bi]_{isoam.\ ac.}/[Bi]_{H_2O}$) in isoamyl acetate as a function of $[I^-]$ at total bismuth concentration $5 \cdot 10^{-4}$ *M* (3.0 *N* sulfuric acid, 3% sodium hypophosphite). Volume aqueous phase 20 ml; volume isoamyl acetate 5 ml.

in iodide. The increase in extractability with increasing acidity is due not only to the repression of hydrolysis of bismuth ion but also to the salting out of bismuth iodide. In 3 *N* perchloric acid and in 5 *N* sulfuric acid, bismuth iodide separated and dissolved slowly in the organic phase on shaking. The complexing of bismuth by the sulfate is clearly shown. Hydrochloric acid can not be used for acidification because of the formation of bismuth–chloride complexes which prevent bismuth extraction.

In Fig. 3 the per cent extraction of bismuth is plotted as a function of the iodide concentration in 3.0 *N* sulfuric acid solution in the presence of 3% sodium hypophosphite, 6% sodium hypophosphite, and an ascorbic acid–sulfite mixture (prepared

fresh daily) such as sometimes used in the spectrophotometric iodide determination of bismuth[4]. The chief feature of interest here is the extractability peak occurring at about 0.0065 *M* KI. This maximum indicates that bismuth is extracted largely, if not entirely, as BiI_3 by isoamyl acetate, so that at the higher iodide concentrations, where anionic iodide complexes of bismuth are being formed, the extraction of bismuth falls off. In Fig. 4, the logarithm of the extraction coefficient (Σ[Bi] isoamyl acetate/Σ[Bi] aqueous) is plotted against the logarithm of the iodide concentration. The two limbs of the curve approximate straight lines. *n*-Amyl acetate gives virtually the same extractability as isoamyl acetate.

Fig. 5 shows the effect of the concentration of bismuth on its extraction with soamyl acetate at three iodide concentrations. At the optimum iodide concentration

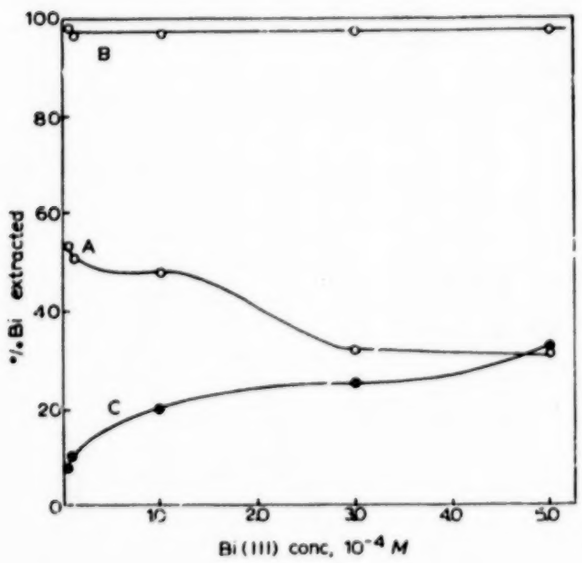

Fig. 5. Extractability of bismuth by isoamyl acetate as a function of bismuth concentration. 20 ml aqueous phase (3.0 *N* sulfuric acid, 3% sodium hypophosphite), 5 ml isoamyl acetate. A, 0.0010 *M* KI; B, 0.0065 *M* KI; C, 0.1000 *M* KI.

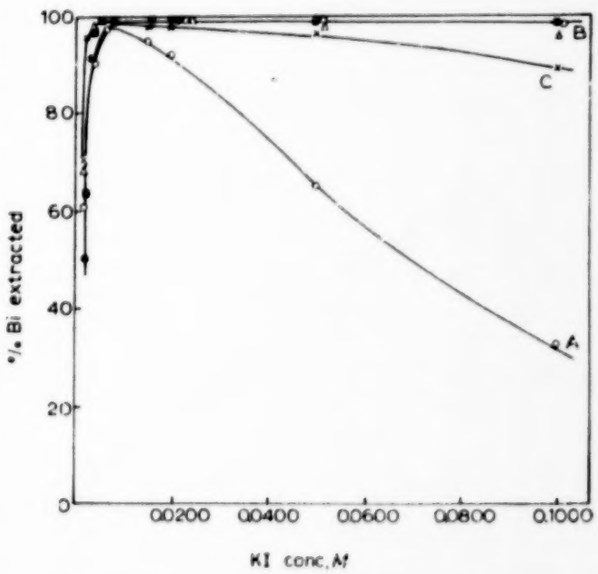

Fig. 6. Extractability of bismuth by isoamyl alcohol, isoamyl acetate, and their mixtures as a function of the iodide concentration. 20 ml aqueous phase (3.0 *N* sulfuric acid, 3% sodium hypophosphite, $5 \cdot 10^{-4}$ *M* Bi) 5 ml organic phase. A(○), isoamyl acetate; B(●), isoamyl alcohol; C(×) 1 isoamyl alcohol: 3 isoamyl acetate; (□) 3 isoamyl alcohol: 1 isoamyl acetate; (△) 1 isoamyl alcohol: 1 isoamyl acetate.

0.0065 *M*) no effect within the limits of experimental error is apparent. At 0.001 *M* odide, the extractability decreases with increasing bismuth concentration, no doubt as the result of the formation of polynuclear bismuth species in the aqueous phase. However, this trend is not shown at the higher iodide concentration of 0.100 *M* where increasing bismuth concentration increases the concentration of molecular bismuth iodide.

In Fig. 6 the extractability of bismuth with isoamyl alcohol and mixtures of isoamyl alcohol and isoamyl acetate is plotted as a function of the iodide concentration. It is clear that isoamyl alcohol extracts iodobismuthous acid as well as bismuth iodide, and the extractability of bismuth remains practically constant at about 99% from 0.015 *M* to 0.10 *M* iodide (the highest concentration tested). At iodide concentrations

less than 0.02 *M*, mixtures of isoamyl alcohol and isoamyl acetate extract bismuth better than either of the pure solvents. This is brought out in Fig. 7, where the extraction for the lower iodide concentrations is plotted. The effect is pronounced at 0.004 *M* I^-, and still sufficiently marked at 0.0065 *M* I^- to make it of possible analytical interest. GOBLE AND MADDOCK[5] found that mixtures of *n*-amyl alcohol and *n*-amyl acetate extract $HPaCl_6$ better than *n*-amyl alcohol alone (*n*-amyl acetate extracts Pa hardly at all), with maximum effect in a *ca.* 1:1 volume ratio. They

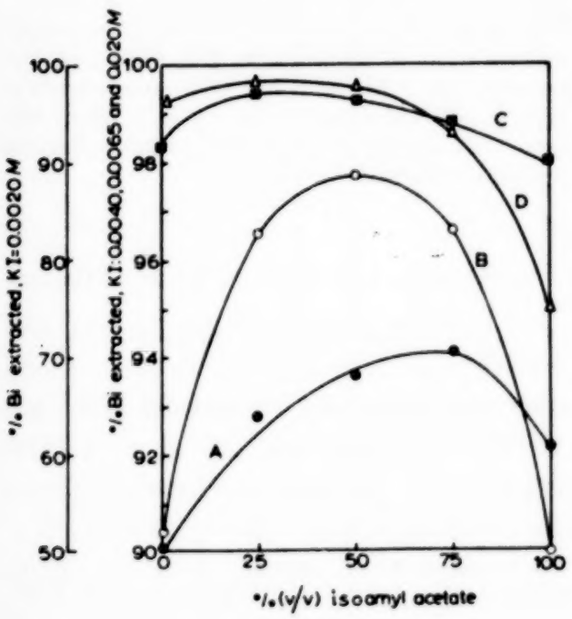

Fig. 7. Extractability of bismuth by isoamyl acetate, isoamyl alcohol and their mixtures at different iodide concentrations. Aqueous phase 3.0 *N* in sulfuric acid, 3% in sodium hypophosphite, and $5 \cdot 10^{-4}$ *M* in bismuth. 20 ml of aqueous phase, 5.0 ml of organic solvent. A, 0.0020 *M* KI; B, 0.0040 *M* KI; C, 0.0065 *M* KI; D, 0.020 *M* KI.

discuss possible reasons for the synergism. In the present case it appears that the synergistic effect is, to a large extent, exerted on the extraction of BiI_3 rather than on $HBiI_4$ or analogous iodo acids.

Determinations of the solubility of bismuth iodide in anhydrous isoamyl alcohol (b.p. 129–31°) and anhydrous isoamyl acetate gave the following average values:

		BiI_3 g/l	BiI_3 *M*
Isoamyl alcohol	25.0°	0.97	0.00165
	31 ± 1°	1.12	0.0019
Isoamyl acetate	25.0°	1.34	0.0023
	31 ± 1°	1.39	0.0024

The concentration of bismuth in the saturated solutions was determined spectrophotometrically by the iodide method so the error in these values may amount to 1–2%, possibly more for the 31° value. The solid phase was analyzed before and after equilibration with the organic solvent and was found to have the theoretical bismuth content for BiI_3. The lower solubility of bismuth iodide in isoamyl alcohol than in isoamyl acetate is reflected in the lower percentage extraction of bismuth by the former solvent from 0.002 *M* iodide solution, in which little anionic bismuth iodide complex can be present.

The behaviour of other elements in the iodide extraction when this is followed by dithizone determination of bismuth will be described elsewhere. It may be noted that

Hg(II), Sb(III), Pb(II), and Tl(III) (the latter if free iodine is present in the system) are partially extracted under the optimum extraction conditions for bismuth. The extraction of lead amounts to 1.6 to 2.0%.

ACKNOWLEDGEMENT

One of the authors, H. A. M., wishes to express his thanks to the University of Buenos Aires, Argentina, for a fellowship held during the course of this work.

SUMMARY

The optimum iodide concentration (excess) for the extraction of bismuth as BiI_3 into isoamyl acetate from 1–5 *N* sulfuric acid solution is approximately $5 \cdot 10^{-3}$ *M*. At this iodide concentration the extraction coefficient [Bi] isoamyl acetate/[Bi]$_{H_2O}$ is approximately 130 (25–30°) when the ratio of isoamyl acetate to aqueous phase is 1 : 4. Mixtures of isoamyl acetate and isoamyl alcohol in the proper ratios extract BiI_3 to a greater extent than either solvent alone.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'extraction du bismuth, sous forme d'iodure (BiI_3), au moyen d'acétate isoamylique et d'alcool isoamylique.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Extraktion von Bismut als Bismutjodid (BiI_3) mit Isoamylacetat und Isoamylalkohol aus wässriger Lösung.

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KOMPLEXOMETRISCHE TITRATION VON VIERWERTIGEM URAN

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EINLEITUNG

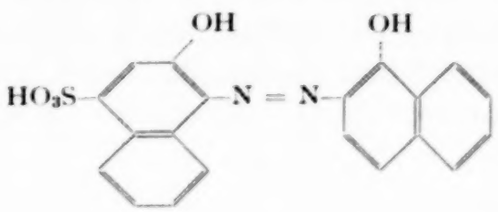
Bei den meisten Verfahren zur Bestimmung von vierwertigem Uran werden Kaliumpermanganat[1–8], Cerisulfat[9–15] und Bichromat[16–18] zu dessen oxydimetrischer Titration verwendet.

Mangels geeigneter Indikatoren konnte bis jetzt noch keine Methode zur direkten komplexometrischen Bestimmung von Uran(IV) gefunden werden. KINNUNEN UND WENNERSTRAND[19] bestimmen vierwertiges Uran durch Zugabe von ÄDTA im Über-

schuss und Rücktitration der überschüssigen ÄDTA-Menge mittels Thoriummasslösung, wobei Xylenolorange als Indikator verwendet wird. LASSNER UND SCHARF[20] entwickelten eine Methode zur komplexometrischen Titration von sechswertigem Uran unter Verwendung von PAN als Indikator.

Die vorliegende Arbeit ist das Ergebnis einer Reihe von Untersuchungen, bei denen eine Anzahl von Azofarbstoffen auf ihre Brauchbarkeit als Metallindikatoren bei der ÄDTA-Titration von Uran(IV) geprüft wurden.

Als am geeignetsten erwies sich der Azofarbstoff, Solochromschwarz 6 BN (Solochrome Black 6BN*) (1-(1-Hydroxy-2-naphthylazo)-2-naphthol-4-sulfonsäure):



Dieser Farbstoff bildet mit Uran(IV) in 0.01 bis 0.2 *N* salzsaurer Lösung einen blaugefärbten Komplex, der durch Zugabe einer ÄDTA-Lösung im Endpunkt der Titration die rote Farbe der Blindlösung annimmt. Da die Komplexbildung mit ÄDTA auch hier wie üblich im Verhältnis 1 : 1 erfolgt, kann diese Reaktion zur quantitativen Bestimmung von vierwertigem Uran herangezogen werden.

Da allerdings die Anzahl der diese Methode störenden Kationen und Anionen sehr gross ist, kann dieses Titrationsverfahren in den meisten Fällen nur nach vorangehender Abtrennung des Urans verwendet werden (s.S. 309).

Mit der hier beschriebenen Methode lassen sich insbesonders Milligrammengen Uran sehr gut und rasch bestimmen, so dass sich dieses Verfahren zur Uranbestimmung in relativ uranreichen Materialien, sowie zur Ermittlung des Uran(IV)-gehaltes von Lösungen, die ausserdem noch Uran(VI)-ionen enthalten, eignen dürfte.

LÖSUNGEN UND REAGENTIEN

Uranstandardlösung

Eine genau gewogene Menge an analysenreinem Uranylnitrat wurde zur Entfernung der Nitrationen einige Male mit Salzsäure auf dem Wasserbad abgedampft. Der aus Uranylchlorid bestehende Rückstand wurde schliesslich in 10 *N* Salzsäure gelöst. Die entstandene Lösung wies einen gravimetrisch überprüften[21] Gehalt von 10 mg Uran(VI)/ml auf. Zur Reduktion des Uran(VI) zu Uran(IV) wurden 10 ml dieser Lösung unmittelbar in einem 100-ml Messkolben mit 2 oder 3 Zinkgranalien *p.a.* versetzt. Nach Ablauf der stürmisch verlaufenden Reduktion, wurde der unverschlossene Kolben zwecks Entfernung der gebildeten Uran(III)-ionen solange umgeschwenkt, bis die rein grüne Farbe der Uran(IV)-ionen sichtbar war (1 bis 2 min). Hierauf wurde mit dest. Wasser zur Marke aufgefüllt. Aus dieser Lösung, die 1 mg Uran(IV)/ml enthielt, wurden dann durch Verdünnen mit 0.1 *N* Salzsäure weitere Standardlösungen hergestellt. Da die Uran(IV)-lösungen unter diesen Bedingungen nur einige Zeit haltbar sind, ist es nötig, sie täglich frisch durch Reduktion der Uran(VI)-lösung herzustellen. Die Reduktion kann selbstverständlich auch unter Verwendung von

* Dieser Farbstoff wurde von dem I.C.I., Hexagon House, Blackley, Manchester, England bezogen. Er scheint sich auch zur spektrophotometrischen Bestimmung von Uran(IV) zu eignen.

Reduktoren wie z.B. eines Jones-Reduktors[1], Blei[9,14]- oder Silberreduktors[15] ausgeführt werden.

Farbstofflösung

Es wurde eine 0.05%-ige methanolische Lösung von Solochromschwarz 6BN verwendet.

ÄDTA-Lösungen

Verwendet wurden 0.1, 0.01 und 0.001 *M* Lösungen des Dinatriumsalzes der Äthylendiaminotetraessigsäure. Die Aufbewahrung der 0.001 *M* ÄDTA-Lösung erfolgte in besonders vorbehandelten Hartglasflaschen[22]. 1 ml 0.1 *M* ÄDTA-Lösung = 23.8 mg Uran und 1 ml 0.001 *M* ÄDTA-Lösung = 238 μg Uran.

Lösungen anderer Elemente

Es wurden wässrige oder 0.1 *N* salzsaure Lösungen sehr vieler Elemente aus *p.a.* Reagentien (Chloride oder Sulfate) hergestellt. Ferner wurden angewendet: Salzsäurelösungen verschiedener Konzentration und Granalien aus Zink *p.a.*

EINFLUSS DER ACIDITÄT, TEMPERATUR UND FARBSTOFFKONZENTRATION

1 ml der Uran(IV)-chloridlösung, die 1 mg Uran/ml enthielt, wurde mit 4 ml 0.1 *N* Salzsäure versetzt und mit dest. Wasser auf 10 ml aufgefüllt. Nach Zugabe von 1 ml der Farbstofflösung wurde die Lösung mittels der 0.001 *M* ÄDTA-Lösung unter Verwendung einer Mikrobürette gegenüber einer auf gleiche Weise bereiteten uranfreien Lösung (Leerwert) titriert. Der Farbumschlag von Blau nach dem Rot des Leerwertes erfolgte unter diesen Bedingungen sehr scharf. Analoge bei anderen Salzsäurekonzentrationen durchgeführte Titrationen ergaben, dass der Farbumschlag im Aciditätsbereich von 0.01 bis 0.2 *N* an Salzsäure am schärfsten war.

Durch Erhöhung der Temperatur wird die Feststellung des Farbumschlags, und zwar insbesonders in der Nähe des Endpunktes gefördert, so dass man gegen Ende der Titration die Lösung im kochenden Wasserbad etwas erwärmen soll.

Bezüglich des Einflusses der Farbstoffkonzentration auf die genaue Ermittlung des Endpunktes wurde festgestellt, dass 1 ml der 0.05%-igen Farbstofflösung/10 ml Titriervolumen die geeignetste Menge ist.

EMPFINDLICHKEIT UND GENAUIGKEIT

Es wurde eine grosse Anzahl von Titrationen nach der beschriebenen Arbeitsvorschrift (s.S. 309) im Milli- und Submilligrammbereich unter Verwendung von 0.1, 0.01 und 0.001 *M* ÄDTA-Lösungen durchgeführt. Die Ergebnisse dieser Titrationen sind aus Tabelle I ersichtlich. Der prozentuelle Titrationsfehler bewegt sich je nach der eingesetzten Uranmenge im Milligrammbereich zwischen $\pm$0.1 bis $\pm$1.0%. Im Submilligrammbereich können schon Fehler bis zu 10% auftreten, so dass diese Methode vor allem zur Bestimmung von Milligrammengen Uran geeignet ist. Das Titriervolumen wurde jeweils so gewählt, dass 1 mg oder weniger Uran(IV)/ml vorhanden war.

TABELLE I

Eingesetzte Menge Uran mg	*Gefundene Menge Uran mg*	*Fehler %*
100.00	100.20	+ 0.2
100.00	100.10	+ 0.1
50.00	50.10	+ 0.2
25.00	24.95	— 0.2
20.00	20.04	+ 0.2
10.00	9.96	— 0.4
10.00	9.94	— 0.6
5.00	5.04	+ 0.8
5.00	5.02	+ 0.4
1.00	1.01	+ 1.0
1.00	0.99	— 1.0
0.50	0.51	+ 2.0
0.50	0.48	— 4.0
0.20	0.20	± 0.0
0.20	0.19	— 5.0
0.10	0.105	+ 5.0
0.05	0.045	—10.0

EINFLUSS VON FREMDIONEN

Folgende Ionen wurden bezüglich ihres Einflusses auf die Urantitration untersucht: Alkaliionen, Erdalkaliionen, Al^{+3}, Sn^{+2}, Pb^{+2}, Bi^{+3}, Cu^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2}, Zr^{+4}, Hf^{+4}, Ti^{+4}, Th^{+4}, V^{+5}, Cr^{+3}, Mo^{+6}, UO_2^{+2}, Mn^{+2}, Fe^{+3}, Fe^{+2}, Co^{+2}, Ni^{+2}, Ag^{+}, Chlorid, Nitrat, Sulfat, Phosphat und Fluorid. Bei den Titrationen kamen jeweils 1 mg Uran und soweit wie möglich 10 mg des Fremdelements in 10 ml Titriervolumen zur Anwendung.

Die Urantitration wird nicht gestört durch folgende Ionen: Alkaliionen, Erdalkaliionen, Al^{+3}, Pb^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2}, UO_2^{+2}, Co^{+2}, Mn^{+2}, Ag^{+}, Chlorid und Sulfat.

Folgende störende Ionen bilden analog zum vierwertigen Uran unter den gewählten Bedingungen mit dem Farbstoff blaue oder violette Komplexverbindungen: Sn^{+2}, Bi^{+3}, Cu^{+2}, Zr^{+4}, Hf^{+4} und Th^{+4}. Bei Anwesenheit der störenden Ionen ist es daher nötig, das Uran vor seiner Reduktion und Titration abzutrennen. Zu diesem Zweck eignet sich die Ätherextraktion des Uranylnitrats[23] und darauffolgender Anionenaustausch über den Ascorbinatkomplex des Urans[24] bzw. noch besser die Abtrennung des Urans aus salzsaurer äthylalkoholischer Lösung unter Verwendung des stark basischen Anionenaustauschers[25] Dowex 1. In beiden Fällen wird schliesslich reinstes Uranylchlorid erhalten, das dann nach erfolgter Reduktion titriert werden kann.

ARBEITSVORSCHRIFT

Die uranhaltige Probe (z.B. Rückstand des nach einer Ionenaustauschoperation erhaltenen reinen Uranylchlorids[24,25]) wird mit insgesamt 10 ml 10 *N* Salzsäure in einen 100-ml Messkolben gebracht und die Reduktion wie für die Standardlösungen beschrieben (S. 307) ausgeführt. Der mit dest. Wasser aufgefüllten Probe wird ein aliquoter Teil entnommen und so verdünnt, dass die Salzsäurekonzentration der Lösung 0.01 bis 0.2 *N* beträgt und die resultierende Lösung nicht mehr als 1 mg Uran/ml

enthält. Hierauf wird auf je 10 ml der Lösung 1 ml der 0.05%-igen Farbstofflösung zugesetzt und die Titration je nach der zu erwartenden Uranmenge mit 0.1, 0.01 oder 0.001 *M* ÄDTA-Lösung gegenüber einem analog hergestellten Leerwert ausgeführt, wobei kurz vor dem Erreichen des Endpunktes die Lösung im kochenden Wasserbad erwärmt wird, worauf bei Fortsetzung der Titration im Endpunkt ein scharfer Umschlag von Blau nach Rot erfolgt. Wird wenig Uran in der Probe erwartet, so kann die Reduktion auch unter Verwendung von entsprechend weniger 10 *N* Salzsäure in 10-, 20-, oder 50-ml Messkolben ausgeführt werden bzw. ein Mikroreduktor z.B. Mikrobleireduktor[14] verwendet werden.

DANK

HERRN PROF. DR. FRIEDRICH HECHT möchte ich an dieser Stelle für seine Unterstützung, die für die Durchführung dieser Arbeit sehr nützlich war, bestens danken.

ZUSAMMENFASSUNG

Es wird eine Methode zur chelatometrischen Titration von Milli- und Submilligrammengen Uran (IV) beschrieben. Für die Endpunktsanzeige wird der Azofarbstoff Solochromschwarz 6BN verwendet, der in 0.01 bis 0.2 *N* salzsaurer Lösung einen blauen Komplex mit Uran(IV) bildet. Der Farbumschlag im Endpunkt erfolgt von blau nach rot. Die Reduktion des Uran(VI) zu Uran (IV) wird mit Zink in stark salzsaurer Lösung ausgeführt.

SUMMARY

A complexometric titration is described for the determination of uranium(IV). Solochrome Black 6BN is used as indicator. The reduction of uranium(VI) is performed with zinc in hydrochloric acid solution.

RÉSUMÉ

Un titrage complexométrique est décrit pour le dosage de l'uranium(IV). On utilise le noir de solochrome 6BN comme indicateur. La réduction de l'uranium(VI) s'effectue au moyen du zinc, en solution chlorhydrique.

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STUDIES OF THE SOLVENT EXTRACTION OF INDIUM OXINATE

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INTRODUCTION

Oxinate extractions

In recent years a number of investigations have been reported concerning the solvent extraction of metal ions from aqueous solutions into organic phases containing oxine. These include studies with over twenty metals[1]. In addition several general theoretical treatments of similar extractions[2] and a few theoretical treatments of oxine extractions have appeared[3–5].

Extraction equations

Quite a number of authors[2,6] have employed the following equation to describe the extraction of metal ions from an aqueous phase into an organic phase containing a chelating agent:

$$E = \frac{K(HR)_0^n}{F(H)^n} \tag{1}$$

In this expression E represents the ratio of total metal concentration in the organic phase to that in the aqueous phase, K designates the extraction constant which is composed of several other more fundamental constants[6], $(HR)_0$ indicates the concentration of the extraction reagent in the organic phase, (H) represents the concentration of hydrogen ion in the aqueous phase, n designates the valence of the metal ion, and F symbolizes a function defined as

$$F = \Sigma K_i(X)^i \text{ with } K_0 = 1 \tag{2}$$

where the K values represent the successive stability constants of water soluble complexes produced by adding a complexing agent X to the aqueous phase, and (X) represents the concentration of free X in the aqueous phase. When no complexing action takes place, the value of F is unity.

If the logarithm of the first equation is taken the following relationship results

$$\log E = \log K + n \log (HR)_0 + n \text{ pH} - \log F \tag{3}$$

and at 50% extraction in systems having organic and aqueous phases of equal volume where $\log E$ becomes zero

$$n \text{ pH}_{1/2} = -\log K - n \log (HR)_0 + \log F \tag{4}$$

in which $pH_{1/2}$ represents the pH value at which 50% extraction occurs. A more detailed treatment of these equations may be found in a recent volume[2] or in a previous paper in this series[6].

Present problem

In the present work the extraction of indium from aqueous solutions into a number of organic solvents containing oxine was studied using both masked and non-masked systems. A masked system is defined as one in which the aqueous phase contains a complexing agent which forms water-soluble complexes with the metal ion. The effects of oxine concentration, masking agent types and concentrations, organic phases, temperature and pH values of the aqueous phase have been investigated.

EXPERIMENTAL PROCEDURES

The chemicals, apparatus, and general procedures employed were essentially those described in previous work[6]. 10-ml portions of the prepared aqueous phases were stirred with 10-ml portions of the organic phases for a minimum time of 5 h. In all cases the indium concentration in the aqueous phase was originally $2 \cdot 10^{-5}$ *M* and was radioactively labelled with ^{114}In to facilitate measurements of the extraction.

TABLE I

DATA AND CALCULATED QUANTITIES FOR INDIUM EXTRACTIONS

System[a,b]	Organic phase	Initial oxine Molar concentration	Composition of aqueous phase[c]		Observed	Calculated	
					$pH_{\frac{1}{2}}$[d]	log K_{ex}	$pH_{\frac{1}{2}}$
1	$CHCl_3$	$1 \cdot 10^{-1}$	$1 \cdot 10^{-1}$	ClO_4^-	1.7		0.8
2	$CHCl_3$	$1 \cdot 10^{-2}$	$1 \cdot 10^{-1}$	ClO_4^-	2.1		1.8
3	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	ClO_4^-	2.8	0.6	
4	$CHCl_3$	$1 \cdot 10^{-3}$[e]	$1 \cdot 10^{-1}$	ClO_4^-	2.8[e]	0.6[e]	
5	$CHCl_3$	$1 \cdot 10^{-4}$	$1 \cdot 10^{-1}$	ClO_4^-	3.9		3.8
6	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{0}$	ClO_4^-	3.2	0.6	
7	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{0}$	CN^-	—[f]		
8	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	CN^-	—[f]		
9	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	CN^-	2.9		
10	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	CN^-	2.8		
11	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	CN^-	2.8		
12	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{0}$	SO_4^{-2}	3.5		3.5[g]
13	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	SO_4^{-2}	3.2		3.2[g]
14	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	SO_4^{-2}	3.0		2.9[g]
15	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	SO_4^{-2}	3.0		2.8[g]
16	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	SO_4^{-2}	2.8		2.8[g]
17	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{0}$	I^-	3.6		3.6[g]
18	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	I^-	3.0		3.0[g]
19	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	I^-	2.8		2.8[g]
20	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	I^-	2.8		2.8[g]
21	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	I^-	2.8		2.8[g]
22	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{0}$	Br^-	3.6		3.7[g]
23	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	Br^-	3.2		3.2[g]
24	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	Br^-	2.9		2.8[g]
25	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	Br^-	2.8		2.8[g]
26	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	Br^-	2.8		2.8[g]

TABLE I (Continued)

System[a,b]	Organic phase	Initial oxine Molar concentration	Composition of aqueous phase[c]		Observed	Calculated	
					$pH_{\frac{1}{2}}$[d]	log K_{ex}	$pH_{\frac{1}{2}}$
27	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{0}$	Cl^-	3.8		3.8[g]
28	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	Cl^-	3.4		3.4[g]
29	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	Cl^-	3.1		2.8[g]
30	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	Cl^-	2.8		2.8[g]
31	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	Cl^-	2.8		2.8[g]
32	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{0}$	CNS^-	4.2		4.3[g]
33	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	CNS^-	3.5		3.5[g]
34	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	CNS^-	3.0		3.0[g]
35	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	CNS^-	2.8		2.8[g]
36	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	CNS^-	2.8		2.8[g]
37	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{0}$	Fo^-[h]	4.6		5.0[g]
38	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	Fo^-	3.5		4.2[g]
39	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	Fo^-	2.8		2.9[g]
40	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	Fo^-	2.8		2.9[g]
41	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	Fo^-	2.8		2.8[g]
42	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{0}$	Ac^-[i]	4.9		5.0[g]
43	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	Ac^-	3.9		3.8[g]
44	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	Ac^-	2.9		2.8[g]
45	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	Ac^-	2.9		2.8[g]
46	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	Ac^-	2.8		2.8[g]
47	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{0}$	Gl^-[j]	5.4		5.5[g]
48	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	Gl^-	4.3		4.3[g]
49	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	Gl^-	3.3		3.1[g]
50	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	Gl^-	2.9		2.9[g]
51	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	Gl^-	2.8		2.8[g]
52	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{0}$	F^-	6.5[k]		6.1[g]
53	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	F^-	4.5		4.8[g]
54	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{0}$	NTA^{-3}[l]	—[m]		
55	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	NTA^{-3}	10.7		
56	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	NTA^{-3}	10.1		
57	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	NTA^{-3}	9.5		
58	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	NTA^{-3}	8.0		
59	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{0}$	$EDTA^{-4}$[n]	—[m]		11.1[o]
60	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	$EDTA^{-4}$	—[m]		10.8[o]
61	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	$EDTA^{-4}$	—[m]		10.5[o]
62	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	$EDTA^{-4}$	—[m]		10.1[o]
63	$CHCl_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-4}$	$EDTA^{-4}$	10.4[p]		9.8[o]
64	C_6H_5Cl	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	ClO_4^-	3.0	0.0	
65	C_6H_5Br	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	ClO_4^-	3.0	0.0	
66	C_6H_6	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	ClO_4^-	3.1	—0.3	
67	CS_2	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	ClO_4^-	3.2	—0.6	
68	$C_6H_5CH_3$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	ClO_4^-	3.3	—0.9	
69	CCl_4	$1 \cdot 10^{-3}$	$1 \cdot 10^{-1}$	ClO_4^-	3.4	—1.2	

[a] All systems were run at 30.0° ± 0.5° except as noted otherwise
[b] All systems contained $2 \cdot 10^{-5}$ *M* indium
[c] Made up to an ionic strength of 0.1 with $NaClO_4$ if necessary
[d] Error about ± 0.1 pH units as noted otherwise
[e] Run at 0.0° ± 1.0°
[f] Precipitate formed in aqueous phase
[g] See reference 8 for stability constants
[h] Formate
[i] Acetate
[j] Glycolate
[k] Error about ± 0.5 pH units
[l] Nitrilotriacetate
[m] No extraction between pH 2.0–10.7
[n] Ethylenediamine-N,N,N′,N′-tetraacetate
[o] See reference 9 for stability constants
[p] Error about ± 0.2 pH units

RESULTS

The experimental results are presented in Table I, defining conditions of the experiments appearing as footnotes. Each system represents at least 12 individual determinations which were plotted as % indium extracted *vs.* final pH. In almost every case, the curves exhibited the predicted S-shaped pattern shown by systems of this character[2].

INTERPRETATIONS

Almost all of the experimental curves of % indium extracted *vs.* final pH had a shape congruent within experimental error with that predicted for a 1:3 indium–oxine chelate complex[2]. Using the data of Systems 3, 4, 6 and 64–69, and assuming F to be unity, eqn. (4) was used to calculate values of log K by using experimentally known values of n, $pH_{1/2}$, and $(HR)_0$. These values of log K are shown in the 6th column of Table I.

Eqn. (4) predicts that a change in the oxine concentration by a factor of 10 should produce a change in $pH_{1/2}$ of 1.0 unit. In Systems 1, 2, 3 and 5, this prediction is tested. In all cases an increase in oxine concentration shifts the $pH_{1/2}$ value to a lower figure. However, the quantitatively predicted magnitude of the shift is realized only in the low oxine concentration region. These results could possibly be explained in terms of the activity coefficients of oxine in chloroform, the activity coefficients deviating more markedly from unity as the concentrations increase.

Various masking agents caused shifts in the $pH_{1/2}$ values as can be seen from Systems 7–63. Using eqn. (4), the value of log K as calculated for System 3, and stability constants as obtained from the literature and footnoted in Table I, values of $pH_{1/2}$ for a number of the masked systems were calculated. These values appear in the 7th column of Table I. In all cases, the qualitative trend of the observed $pH_{1/2}$ values was as predicted, and in most cases quantitative agreement was also good. An exact comparison between observed and calculated values of $pH_{1/2}$ was not possible in many instances because the calculated values had been obtained by using stability constants which were measured at ionic strengths markedly different from that employed in this study. A comparison of Systems 3 and 6 shows that this variable is a significant one even in non-masked systems, and it is well known that apparent stability constants of various complexes change considerably with ionic strength[7].

Systems 64–69 illustrate the effects of altering the organic phase upon the observed $pH_{1/2}$. It is interesting that in these results as well as in other previous work of this type, none of the organic solvents shifted the $pH_{1/2}$ greater than 1.6 unit[5,6,10].

Systems 3 and 4 present data showing the effect of temperature lowering on the simple non-masked system. Experimentally the situation appears to be temperature independent in the range covered. Thus for the overall extraction reaction the free energy change is about −0.8 kcal/mole, the enthalpy change is zero, and the entropy change is about 3 e.u.

SUMMARY

An investigation of the extraction of radio-labelled $2 \cdot 10^{-5}$ M indium from various aqueous solutions into a number of organic solvents containing oxine has been carried out. The effects of pH value, oxine concentration, masking agents, different organic phases, and temperature have been studied. Extraction constants and pH values of 50% extraction have been measured and compared with theoretically-calculated values.

RÉSUMÉ

Des recherches ont été effectuées sur l'extraction de l'indium sous forme d'oxinate, dans divers solvants organiques. On a examiné l'influence du pH, de la concentration en oxine, des réactifs complexants, des différentes phases organiques et de la température.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Extraktion von Indium aus wässrigen Lösungen mit oxinhaltigen organischen Lösungsmittel unter verschiedenen Bedingungen (Einfluss von pH, Oxin Konzentration, Komplexbildner, verschiedene organische Phasen und Temperatur).

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THE DETERMINATION OF ANTIMONY(III) AND FREE HCl IN MIXTURES

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In the course of an investigation on the extraction of antimony trichloride from hydrochloric acid solutions by tributyl phosphate[1], it was necessary to determine the free hydrochloric acid co-extracted with the trichloride. No method suitable for this purpose could be found in the literature, hence an attempt was made to develop one.

According to COETZEE[2], antimonyl tartrate reacts quantitatively with alkali in a boiling solution,

$$2\ KSbC_4H_4O_6 + 2\ MOH \rightarrow Sb_2O_3 + 2\ MKC_4H_4O_6 + H_2O \qquad (1)$$

SAMANTORA and co-workers[3], on the other hand, concluded that the reaction between antimony trichloride and the tartrate ion releases two equivalents of free acid per atom of antimony according to the reaction:

$$SbCl_3 + C_4H_4O_6^{-2} + H_2O \rightarrow SbOC_4H_4O_6^{-} + 2\ H^+ + 3\ Cl^- \qquad (2)$$

This observation appears to be due to the fact that these workers did not proceed beyond a pH of 3, nor did they use the boiling temperature which was found essential for the complete reaction of antimonyl tartrate by COETZEE.

In the present work, an attempt was made to combine the above two observations and to set up optimum conditions for the complete reaction of antimony trichloride with alkali. It was found that complete reaction is possible not only in the presence of tartrate but also in its absence according to the following equation,

$$2\ SbCl_3 + 6\ MOH \rightarrow Sb_2O_3 + 6\ MCl + 3\ H_2O \qquad (3)$$

Based on these observations, a method has been developed for the alkalimetric determination of antimony trichloride. If a mixture of antimony trichloride and hydrochloric acid is taken, the alkali titre gives the total amount of free acid and trichloride. Analysis of the same solution for antimony(III) by iodimetric titration[4] then enables one to calculate the acid originally present in the mixture.

EXPERIMENTAL

Antimony trichloride–tartrate solution. A weighed amount of pure anhydrous $SbCl_3$

was dissolved in the minimum amount of 10% Rochelle salt solution. The solution was diluted and stored in a bottle attached to a delivery burette from which aliquots were measured and standardised against decinormal iodine solution[4].

Tartar emetic solution. A 5.0% (w/v) solution was prepared in boiling water. It was cooled, diluted to a calculated volume and standardised with iodine.

Antimony trichloride in acetone. A weighed quantity of pure anhydrous $SbCl_3$ was dissolved in pure anhydrous acetone (E. Merck). The solution was kept in a vessel out of contact of air. Aliquots were measured from a delivery burette and standardised against iodine.

Solutions of known antimony content were treated with sufficient water and titrated directly with standard decinormal alkali in presence of phenolphthalein. On titration in the cold, the end-point was not very sharp and the end-reaction was slow. Titration of a boiling solution gave a very sharp end-point. Equally satisfactory results were obtained if larger amounts of the acid were first neutralised in the cold and the titration completed with a boiling solution; this proved to be more convenient. Mixtures containing known amounts of HCl and $SbCl_3$ were likewise titrated.

For the final analysis of such mixtures, after alkalimetric titration, the solution was treated with solid potassium hydrogen tartrate and boiled till the precipitated trioxide, Sb_2O_3, completely dissolved. The solution was then cooled to room temperature and treated with an excess of sodium bicarbonate till sufficiently alkaline. It was then titrated with standard decinormal iodine solution in presence of starch as indicator.

RESULTS AND DISCUSSION

Alkalimetric titration of tartar emetic and antimony trichloride

A number of determinations were carried out with varying amounts of tartar emetic (1.50 to 3.00 mmoles) and antimony trichloride (0.22 to 2.10 mmoles) in separate experiments. With tartar emetic, the alkali consumption was equimolecular, which confirms the earlier observations of COETZEE[2]. With antimony trichloride and tartrate, the alkali consumption was three moles for each mole of the trichloride. This indicates that the trichloride first reacts with tartrate according to equation (2), releasing two moles of acid. The alkali neutralises this first and then reacts further with the antimonyl tartrate, so that the overall reaction requires three moles of alkali for each mole of trichloride.

Some titrations were done with solutions of antimony trichloride in acetone. Here also, under the experimental conditions, sharp end-points were obtained and the molar ratio of alkali to trichloride was 3:1. The presence of tartrate was therefore unnecessary for the success of the method and the hydrolysis of the trichloride proceeds to completion according to equation (3).

Determination of antimony trichloride in presence of hydrochloric acid

After the method had been found suitable for antimony trichloride and tartar emetic taken separately, mixtures of known amounts of the trichloride and hydrochloric acid were titrated with standard alkali. The alkali titre corresponded to the sum of the acid present originally and that liberated from the trichloride. Wide variations in the concentration of acid and trichloride (0.05 to 0.15 g) did not affect the results, which were accurate to $\pm 1.0\%$ for the antimony content.

Final experiments with solutions containing both antimony trichloride and hydrochloric acid

After the method had been standardised, mixtures of antimony trichloride and hydrochloric acid were analysed for both antimony and acid. First, the entire solution was titrated with alkali when the alkali consumed gave the total of acid and trichloride. The same solution was then titrated with iodine according to the method given earlier. This gave the amount of antimony(III), and hence of the trichloride. The free acid present originally in the mixture could then be easily calculated. Variations in the proportions of antimony trichloride (0.1170 to 0.3510 g) and acid (0.0681 to 0.1363 g) did not influence the results. An accuracy of $\pm$ 1.0% for both antimony and acid could be obtained.

When TBP solutions were used, a measured volume was treated with excess of water and the titration performed in the same way as with aqueous solutions.

ACKNOWLEDGEMENT

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SUMMARY

Antimony trichloride in a boiling aqueous solution reacts quantitatively with alkali yielding the trioxide Sb_2O_3. This can be employed for alkalimetric titration of antimony trichloride. When the method is combined with the iodimetric titration of antimony(III), free hydrochloric acid can be determined in presence of the trichloride.

RÉSUMÉ

Une méthode est proposée permettant de doser à la fois $SbCl_3$ et HCl. On procède d'abord à un titrage alcalimétrique de ces deux composés; puis on dose l'antimoine seul, dans la même solution, par titrage avec l'iode. On peut calculer ensuite la teneur en HCl.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur gleichzeitigen Bestimmung von $SbCl_3$ und HCl durch alkalimetrische Titration; das Antimon wird jodometrisch bestimmt.

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THERMOGRAVIMETRIC DETERMINATION OF ETHYLENEDIAMINE AND QUININE WITH DILITURIC ACID

SOLUBILITIES OF SOME POLYMETHYLENEDIAMINE DILITURATES

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In a previous paper the determinations of magnesium, potassium and lead by precipitation with dilituric acid have been described by us[1]. The use of dilituric acid has been extended to the determination of organic bases in this paper. Methods for the determination of ethylenediamine and quinine are presented together with the determination of the solubilities of some polymethylenediamine dilituratés. The thermolysis curves of these compounds are also given.

The organic salts of dilituric acid prepared above can be easily converted back to the original base by reaction with ammonia or magnesium solutions, thus affording a method for their separation[2].

THERMOLYSIS CURVES

The thermal stabilities of the organic salts of dilituric acid are more essential for their determinations than the thermal stabilities of the inorganic salts of dilituric acid, since in the latter case the cation can be eventually determined as the metal oxide at higher temperatures.

Consequently the thermolysis curves of the dilituratés of quinine, ethylenediamine and the polyethylenediamines, have been recorded as well as the thermolysis curve of trimethylamine dilituratе. Trimethylamine dilituratе has been used previously by us[1] for the preparation of a reagent solution, more concentrated than dilituric acid solution, for the quantitative precipitation of potassium.

Experimental

Equipment

An ADAMEL recording thermobalance (Chevenard system) was used to obtain the thermolysis curves.

Salts of dilituric acid

Ethylenediamine dilituratе (EnD_2). Saturated dilituric acid solution in 50% ethanol was added in excess to a $4 \cdot 10^{-2}$ molar solution of aqueous ethylenediamine prepared by dilution with water of ethylenediamine from Eastman Organic Chemicals. Ethylenediamine dilituratе crystals formed after a few seconds. The solution was cooled, the precipitate filtered, washed with 95% ethanol, and dried in an electric furnace at 100° for one hour.

Quinine dilituratе. Saturated dilituric acid solution in 50% ethanol was added in excess to a 10^{-2} *M* solution of quinine, from Pfizer Co., in 50% ethanol. The resultant mixture was heated and then slowly cooled. Large crystals of quinine dilituratе dihydrate formed during the cooling. REDEMANN AND NIEMANN[2] reported in their solubility determinations a molecular weight of quinine dilituratе corresponding to the monohydrate. The solution was finally cooled in an ice bath, the precipitate filtered, washed with 95% ethanol and dried in air in vacuo (a water pump).

Trimethylamine dilituratе (TMAD). The preparation has been described elsewhere[1].

Trimethylenediamine dilituratе ($TMDAD_2$); Tetramethylenediamine dilituratе ($TeMDAD_2$); Pentamethylenediamine dilituratе ($PMDAD_2$). They were all prepared by similar methods. Solutions of hot saturated dilituric acid in water at 25° were added in excess to the hot solutions of the corresponding diamines, from Columbia Organic Chemicals, diluted ten-fold with water. The resultant solutions were allowed to cool slowly. Large crystals of the polymethylenediamine dilituratеs precipitated. The solutions were finally cooled in an ice bath. The precipitates were filtered, washed with water, and left to dry overnight in air.*in vacuo* (a water pump).

Carbon and hydrogen analyses of the above compounds are as follows:

	Calculated	*Found*
Ethylenediamine dilituratе $C_2N_2H_8(C_4N_3H_3O_5)_2$ mol. wt. 406.3	C: 29.78%; H: 3.47%	C: 29.45%; H: 3.49% 29.81% 3.19%
Trimethylamine dilituratе $C_3NH_9(C_4N_3H_3O_5)$ mol. wt. 233.2	C: 36.22%; H: 5.21%	C: 36.04%; H: 5.49% 35.81% 5.41%
Trimethylenediamine dilituratе monohydrate $C_3N_2H_{10}(C_4N_3H_3O_5)_2 \cdot H_2O$ mol. wt. 438.4	C: 30.14%; H: 4.15%	C: 32.01%; H: 4.82% 31.90% 4.67%
Tetramethylenediamine dilituratе trihydrate $C_4N_2H_{12}(C_4N_3H_3O_5)_2 \cdot 3H_2O$ mol. wt. 488.4	C: 29.51%; H: 4.96%	C: 32.01%; H: 4.82% 31.90% 4.67%
Pentamethylenediamine dilituratе trihydrate $C_5N_2H_{14}(C_4N_3H_3O_5)_2 \cdot 3H_2O$ mol. wt. 502.5	C: 31.07%; H: 5.23%	C: 30.75%; H: 5.11% 30.89% 5.33%
Quinine dilituratе dihydrate $C_{20}N_2H_{24}O_2(C_4N_3H_3O_5)_2 \cdot H_2O$ mol. wt. 706.7	C: 47.58%; H: 4.86%	C: 47.68%; H: 4.97% 47.49% 4.75%

The hydrates of tri- and tetramethylenediamine dilituratеs are quite unstable towards heat, probably accounting for the discrepancies in the results obtained for these two compounds.

The crystalline nature of the organic salt dilituratеs prepared above renders their identification by X-ray powder diffraction methods very easy[3].

Method

The thermolysis curves were obtained by heating the dilituratеs in No. 000 porcelain crucibles. The weights of the samples and the rates of heating are given in Figs. 1 and 2. All samples were heated in a stream of dry nitrogen flowing at the rate of 2 l/h.

Results and discussion

The thermal decomposition curves of ethylenediamine, tetramethylenediamine and quinine dilituratesare shown in Fig. 1 and those of trimethylamine and trimethylenediamine dilituratesin Fig. 2.

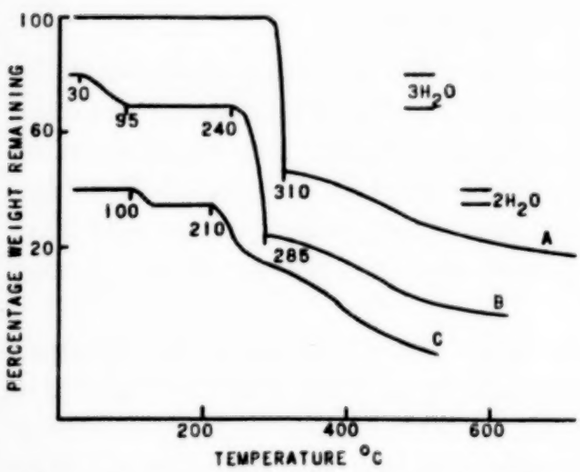

Fig. 1. Thermolysis curves of organic dilituratesA. Ethylenediamine dilituratesA, 113.6 mg heated at 150°/h; B. Tetramethylenediamine dilituratesA, 120.3 mg heated at 150°/h; C. Quinine dilituratesA, 17.0 mg heated at 150°/h.

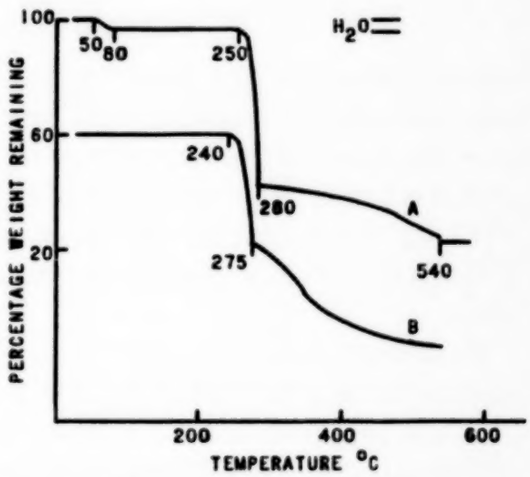

Fig. 2. Thermolysis curves of organic dilituratesA. Trimethylenediamine dilituratesA, 124.9 mg heated at 150°/h; B. Trimethylamine dilituratesA, 214.9 mg heated at 65°/h.

The diamine salts of dilituric acid, with the exception of ethylenediamine, formed hydrates which dehydrated below 100°. The anhydrous salts of dilituric acid studied here were stable to 240° at least. The decompositions which followed were abrupt, except in the case of quinine dilituratesA. At 270° the compounds had not yet completely decomposed but thermolysis was not carried above that temperature.

Ethylenediamine dilituratesA was stable to 290° on heating. An abrupt decomposition followed leaving only 46% of the initial weight. The residue decomposed slowly to 720° where only 15% of the weight remained.

Trimethylenediamine dilituratesA monohydrate ($TMDAD_2$) dehydrated between 50° and 80°; the anhydrate was stable to 250°. An abrupt decomposition followed, leaving 42% of the initial weight. The rest of the decomposition was similar to that of ethylenediamine dilituratesA.

Tetramethylenediamine dilituratesA trihydrate ($TeMDAD_2$) dehydrated between 30 and 95°; the anhydrate was stable to 240°. After a fast decomposition to 285° leaving 44% of the initial weight there was a decomposition similar to that of ethylenediamine.

The decomposition curve of pentamethylenediamine dilituratesA trihydrate ($PMDAD_2$) is not represented graphically but is very similar to that of $TeMDAD_2$. Dehydration took place between 40 and 105°. The anhydrous salt was stable to 250°. Fast decomposition to 275° left 40% of the initial weight.

Trimethylamine dilituratesA ($TMAD$) was stable to 240°. There an abrupt decomposition left 60% of the initial weight. Further decomposition resembled that of ethylenediamine.

Quinine dilituratesA dihydrate dehydrated between 100–130°. The anhydrous com-

pound was stable to 210°. The decomposition of the organic part was not abrupt as in the case of the amine dilituratcs. At 550°, 42% of the initial weight remained undecomposed.

The semistable intermediates which formed by the abrupt decomposition of the amine dilituratcs had an apparent molecular weight of about 200.

DETERMINATION OF ETHYLENEDIAMINE

Ethylenediamine like most organic compounds usually has been determined by measurement of properties of its functional groups and not by a unique characteristic as is the case with many inorganic ions. The only gravimetric method thus far reported is based on precipitation of the insoluble double salt $UO_2(HSO_4)_2-(NH_2(CH_2)_2-NH_2)$ by RAURICH SAS[4]. It has the advantage that many other amines (CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, antipyrine, morphine, quinine and strychnine) are not precipitated.

REDEMANN AND NIEMANN[2] have given the solubility of ethylenediamine dilituratc in water to be $4\cdot10^{-4}$ *M* at 25°. Only magnesium dilituratc, among all the dilituratcs, has been reported to have a lower solubility. The determination of ethylenediamine by precipitation with dilituric acid should be feasible not only because of its solubility but also because of its good thermal stability.

Experimental

Reagents

Ethylenediamine. An ethylenediamine solution was prepared by diluting anhydrous ethylenediamine, from the Matheson Co., with distilled water and standardizing by titration with a HCl solution previously standardized against Na_2CO_3, using mixed indicator (1.4 g xylene cyanole F.F., 1.0 g methyl orange per 100 ml solution) for the detection of the end-point. The solution analyzed 1.103 mg of ethylenediamine/ml.

Methylamine. The methylamine solution from the Matheson Co. was prepared and standardized in the same manner as the ethylenediamine solution. It was found to be $4.75\cdot10^{-2}$ *N*.

Dilituric acid. The precipitation solution of dilituric acid was prepared similarly to the one used for the determination of magnesium[1].

Method

The procedure for precipitation and washing of ethylenediamine dilituratc was similar to the one used for magnesium dilituratc[1]. 10-ml samples of ethylenediamine were treated with 30 ml of dilituric acid solution. This corresponded to a 4- to 1-excess of equivalents of dilituratc ions over ethylenediamine. The precipitate obtained was dried in the thermobalance between 230° and 260°. A constant weight was obtained within 10–15 min. The precipitate corresponded to ethylenediamine dilituratc hemihydrate.

Analytical results

In Table I we have the results for the determination of ethylenediamine obtained by this method. Results showing the interference of methylamine in the determination of ethylenediamine are shown in Table II.

TABLE I

THERMOGRAVIMETRIC DETERMINATION OF ETHYLENEDIAMINE

Ppt. (mg)	*En found (mg)*	*Deviation (mg)*	*Remarks*
75.2	10.88	—0.15	No cooling
75.4	10.91	—0.12	No cooling
74.6	10.79	—0.24	No cooling
75.5	10.92	—0.11	No cooling
75.5	10.93	—0.10	No cooling
76.0	11.00	—0.03	No cooling
75.7	10.96	—0.07	Cooling
76.6	11.09	+0.06	Cooling
76.3	11.04	+0.01	Cooling
75.4	10.92	—0.11	Cooling
76.2	11.03	+0.00	Cooling
76.7	11.10	+0.07	Cooling
76.3	11.03	0.00	Cooling
76.3	11.03	0.00	Cooling
76.1	11.01	—0.02	Cooling
11.03 mg of En were taken in the above determinations			
14.4	2.08	—0.13	Cooling
15.7	2.27	+0.06	Cooling
15.6	2.27	+0.05	Cooling
15.4	2.22	+0.01	Cooling
2.21 mg of En were taken in the above determinations			

TABLE II

INTERFERENCE OF METHYLAMINE IN THE ETHYLENEDIAMINE DETERMINATION

Concentration (M)	*Excess ppt.*	*Weight $MeNH_2$ in mg*	
		taken	*found*
$2.5 \cdot 10^{-3}$	0	2.94	0
$5 \cdot 10^{-3}$	0	5.88	0
$1.4 \cdot 10^{-2}$	118.8	29.4	18.8
$2.2 \cdot 10^{-2}$	295.3	73.4	46.5
11.03 mg of En were present in each of these determinations			

Discussion of results

For our experimental conditions with a four fold excess of precipitant using the solubility product of ethylenediamine diliturate[2] we calculate that only $4 \cdot 10^{-3}$ mg of ethylenediamine should remain dissolved in the 40 ml of solution at 25°.

Nevertheless the average deviation for the 6 samples each containing 11.03 mg of ethylenediamine which were not cooled in ice before filtration is —1.2% while for the 8 samples which were cooled the deviation is only —0.1%.

The solubility product of methylamine diliturate is $1.4 \cdot 10^{-3}$; a concentration of methylamine over $5 \cdot 10^{-2}$ moles/l is necessary, for our experimental conditions with 10 ml of ethylenediamine solution, for the solubility product of methylamine diliturate to be exceeded.

It is found that when the concentration of methylamine is less than that of ethylenediamine, methylamine will not interfere. Above this concentration and even when the

concentration of methylamine is three times lower than the concentration necessary for the solubility product to be exceeded we have precipitation of methylamine on the ethylenediamine dilituratе precipitate.

Quantities of 2 to 11 mg of ethylenediamine can be determined gravimetrically by precipitation with dilituric acid in presence of concentrations of methylamine not exceeding those of ethylenediamine. The accuracy is of the order of 1%.

DETERMINATION OF QUININE

Acid titration is the most common method for the evaluation of the quinine content of solutions, but these methods[5-7] are not very specific.

Purely gravimetric methods also have been described. SHIMOKAWA[8] precipitated quinine as a flavionate in ethyl acetate solution, and BESSON AND BRIGNON[9] as $(SbI_3)_2 \cdot$ (quinine) $2H_2O$. Nitranilic acid has been used for the precipitation of quinine by BORGWARDT[10], but many other alkaloids interfere. SHIOKAWA[11] precipitated quinine with silicotungstic acid and then ignited the precipitate on the thermobalance to $SiO_2 \cdot 12\ WO_3$ for the final determination.

We have studied the determination of quinine by precipitation as quinine dilituratе. Its separation from strychnine and cinchonine has also been investigated. The paper by REDEMANN AND NIEMANN[2] indicates that the solubility products of strychnine and cinchonine dilituratеs are respectively 10 and 100 times larger than that of quinine dilituratе and thus should render this separation possible.

Experimental

Reagents

Dilituric acid solution. A 0.02-*M* solution in 40% ethanol was prepared by dissolving an excess of dilituric acid in a heated solution, cooling it then to room temperature, and filtering off the excess dilituric acid.

Quinine solution. Quinine, from Merck Chemicals, was weighed and dissolved in a 50% ethanol solution. The dissolution was helped by heating. Upon cooling the solution was brought to volume with 50% ethanol. Solution A was $3.12 \cdot 10^{-3}$ *M*; solution B, $1.24 \cdot 10^{-2}$ *M* and solution C, $1.22 \cdot 10^{-3}$ *M*. The solution B of quinine was titrated with standard HCl, previously standardized against Na_2CO_3. It gave a normality of $1.24 \cdot 10^{-3}$.

Cinchonine solution. Cinchonine, from Merck Chemicals, was weighed and dissolved in 95% ethanol. The dissolution was helped by heating. Upon cooling the solution was brought to volume with additional 95% ethanol. Solution A was $1.62 \cdot 10^{-3}$ *M* and solution B $2.72 \cdot 10^{-2}$ *M*.

Strychnine solution. Strychnine, from Pfizer, was weighed and dissolved in 95% ethanol. The dissolution was helped by heating. Upon cooling the solution was brought to volume with additional 95% ethanol. This solution was $1.64 \cdot 10^{-2}$ *M*.

Method

5-ml aliquots of the quinine B solution were treated with 10 ml of the dilituric acid solution. Other volumes and concentrations of quinine were treated with proportionate volumes of reagent so that a molar ratio of dilituric acid/quinine of around 7/1 was used. The quinine dilituratе dihydrate precipitate was allowed to form at room temperature for 1 to 2 h to insure the formation of large crystals. The solution was cooled

in ice and filtered on a glass fritted filter of medium porosity. The precipitate was washed with a small amount of ice cold 50% ethanol saturated dilituric acid solution, and finally twice with cold 95% ethanol. For the thermogravimetric determination the sintered glass filter containing the precipitate was placed on the thermobalance, preheated to a temperature between 140 and 195°. A constant weight was obtained within about 15–20 min, corresponding to the anhydrous quinine dilituric acid.

The crucible with the precipitate should be introduced slowly and gradually in the furnace, in order to prevent a fast initial dehydration from producing an impermeable coating of the anhydrous compound rendering further dehydration difficult.

Analytical results

In Table III we have the results for the determination of quinine obtained by this method.

TABLE III

THERMOGRAVIMETRIC DETERMINATION OF QUININE

Quinine taken (mg)	*Conc. quinine (mg/ml)*	*Quinine found (mg)*	*Deviation (mg)*
1.98	0.395	1.97	−0.01
2.01	0.395	2.09	+0.08
3.95	1.34	3.92	−0.03
4.01	4.01	4.16	+0.15
4.01	1.34	3.86	−0.15
8.02	3.21	7.94	−0.07
8.02	2.67	8.13	+0.13
8.02	2.87	7.69	−0.33
10.12	1.012	10.09	−0.03
11.04	4.01	16.68	+0.64
20.06	4.01	20.90	+0.84
20.06	2.01	19.79	−0.27
34.23	1.37	33.49	−0.74
38.28	1.53	37.22	−1.06
5.06 (dihydrate)	1.012	5.22	+0.16

TABLE IV

CINCHONINE INTERFERENCE IN THE QUININE DETERMINATION

Quinine taken (mg)	*Quinine found (mg)*	*Quinine (mg/ml)*	*Cinchonine taken (mg)*	*Concentration cinchonine (mg/ml)*	*Deviation (%)*
8.02	7.64	3.21	0.24	0.10	−4.7
8.02	7.81	2.67	0.48	0.16	−2.6
8.02	7.68	2.86	6.40	2.29	−4.2
8.02	7.95	2.29	12.01	3.43	−0.9
8.02	9.26	2.01	16.01	4.00	+15.4
12.03	11.58	2.41	16.01	3.20	−3.7
12.03	13.58	2.01	24.02	4.00	+12.5
16.04	15.26	2.29	24.02	3.43	−4.8

Discussion

Quantities of quinine between 2 and 40 mg have been determined with a maximum deviation of 3%. This determination was possible for concentrations of quinine above 0.4 mg/ml. Below such concentrations the negative error was very large.

Using the solubility of quinine dilituratе in water given by REDEMANN AND NIEMANN[2] we have calculated that for a quinine solution of 0.158 mg/ml conc. (7.9 mg sample) to which 10.0 ml of 0.02 *N* dilituric acid has been added there should be no precipitate since the solubility product is not exceeded. Experimentally in a 50% ethanol solution 40% of the total precipitate forms. This shows that the solubility product is not lowered enough by addition of ethanol for the determination of such low concentrations of quinine to be possible.

Cinchonine and strychnine interferences

Table IV shows that at concentrations below 3.5 mg/ml of cinchonine no coprecipitation is taking place. Solubility calculations show that cinchonine has no tendency for coprecipitation and will begin interfering only when its solubility product is exceeded.

Table V shows that at concentrations below 1.0 mg/ml of strychnine there is little or no interference in the determination of quinine. Solubility calculations show that strychnine interfered only when the solubility product of strychnine dilituratе is largely exceeded.

TABLE V

STRYCHNINE INTERFERENCE IN THE QUININE DETERMINATION

Quinine taken (mg)	*Quinine found (mg)*	*Theor. conc. quinine (mg/ml)*	*Strychnine taken (mg)*	*Conc. strychnine (mg/dl)*	*Deviation (%)*
8.02	8.19	3.21	2.74	1.10	+2.1
8.02	8.28	2.29	8.23	2.35	+3.2
8.02	11.72	1.60	16.46	3.29	+46.1
12.03	11.91	3.01	5.49	1.37	—1.0

Conclusion

The presence of a large excess of dilituric acid is necessary in order to achieve complete precipitation of quinine dilituratе. The use of a 40% ethanol solution of trimethylamine dilituratе as a precipitating solution was a complete failure, in spite of the higher concentration of dilituratе ions, since the precipitate did not even form. The separation of quinine from cinchonine and strychnine by precipitation as the dilituratе is good up to moderate concentrations of these two alkaloids.

DETERMINATION OF THE SOLUBILITIES OF SOME POLYMETHYLENEDIAMINE DILITURATES IN WATER AT 0° AND 25°

In the middle of the last century qualitative accounts of the solubilities of dilituratе salts were given by SCHLIEPER[12] and BAEYER[13]. REDEMANN AND NIEMANN[2] are the only ones to date to report the quantitative determination of the solubilities of dilituratеs salts. In the present work, we have determined the solubilities of the dili-

turates of ethylenediamine, trimethylenediamine, tetramethylenediamine and pentamethylenediamine in water at 0° and 25°.

Experimental

Reagents

The preparation of the polymethylenediamine dilituratés has been described above.

Method

100 to 150 mg of the polymethylenediamine diliturate were placed in a 100-ml volumetric flask; 60 to 80 ml of warm water were added and the flask shaken for several min. The flask was then immersed either in an ice bath at 0° or in a constant temperature bath at 25°. Both these temperatures were maintained within ±0.2°.

The solutions were mechanically shaken for about 15 h; a portion was then filtered very rapidly through a No. 42 Whatman filter paper in a Buchner funnel (cooled with ice when filtering the 0° solutions). 10-ml aliquots were pipetted into previously weighed weighing bottles and the solvent evaporated off at as low a temperature as possible in an electric furnace: EnD_2 at 120°; $TMDAD_2$ at 95°; $TeMDAD_2$ at 95°; and $PMDAD_2$ at 120°. (These were the minimum temperatures necessary to obtain the anhydrous compounds as determined from the thermolysis curves). Five to eight hours were necessary for evaporation to dryness. Duplicate runs were made.

Results and discussion

The solubilities of the polymethylenediamine dilituratés are given in Table VI for 0° and 25° together with the ionization constants of these compounds at 25°.

REDEMANN AND NIEMANN[2] claimed that 48 h were necessary in order to achieve equilibrium in solution; we have found that 12 h were sufficient.

It can be seen from the thermolysis curves that the temperature of 80° used by REDEMANN AND NIEMANN for the evaporation was too low in the case of the polymethylenediamine dilituratés in order to obtain the anhydrous forms.

REDEMANN AND NIEMANN[2] pointed out that within limits the solubility in water of primary aliphatic amine dilituratés increases with chain length. In studying the solubility values given by these authors we found that this increase in solubility with chain length occurs also with aliphatic dilituratés of mono amino carboxylic acid.

It was also noticed from their data that the more basic acids give the most insoluble

TABLE VI

SOLUBILITIES OF SOME POLYMETHYLENEDIAMINE DILITURATES AT 0° AND 25°

Compound	*Solubility in mmoles/l* 0°	25°	*Ioniz. const.*[14] *of the diamine* pK_1	pK_2
Ethylenediamine diliturate	0.11	0.47	9.87	6.80
Trimethylenediamine diliturate	0.69	2.13	10.30	8.29
Tetramethylenediamine diliturate	0.25	0.96	10.19	8.78
Pentamethylenediamine diliturate	0.74	2.65	10.25	9.13

dilturate compounds and that amino acids having an ionizable hydroxyl group gave very insoluble diliturates and that this insolubility increased with increasing strength of the hydroxyl acid group. Among alkaloids having practically the same structure, the more basic ones gave the more soluble diliturates in contrast to the amino-acids.

For the series of polymethylenediamine diliturates mentioned above we can predict a general trend for the increase in solubility with increasing number of carbon atoms. The ionization constant of trimethylenediamine is higher than would be expected from a gradual increase in the chain length[14].

From our experimental data (Table VI) we see that this anomaly enhances the solubility of trimethylenediamine rendering it more soluble than the tetramethylenediamine diliturate.

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SUMMARY

The thermolysis curves of ethylenediamine, trimethylenediamine, tetramethylenediamine, pentamethylenediamine, trimethylamine and quinine diliturates were determined. These curves established that either the hydrated or the anhydrous form of ethylenediamine and quinine diliturate is stable enough for their gravimetric use to be possible. Both ethylenediamine and quinine were determined by precipitation with alcoholic dilituric acid solution. In addition the solubilities of some polymethylenediamine diliturates were determined.

RÉSUMÉ

Les auteurs ont établi les courbes de thermolyse des diliturates d'éthylènediamine, de triméthylènediamine, de tétraméthylènediamine, de pentaméthylènediamine, de triméthylamine et de quinine. Les diliturates d'éthylènediamine et de quinine sont suffisamment stables pour être utilisés en gravimétrie. La solubilité de quelques diliturates de polyméthylènediamine a été déterminée.

ZUSAMMENFASSUNG

Beschreibung des thermolytischen Verhaltens der Diliturate von Aethylendiamin, Trimethylendiamin, Tetramethylendiamin, Pentamethylendiamin, Trimethylamin und Chinin; unter diesen sind die Diliturate von Aethylendiamin Chinin genügend stabil um zur gravimetrischen Bestimmung dieser Verbindungen verwendet werden zu können. Es wurde weiterhin die Löslichkeit einer Anzahl Polymethylendiamin-diliturate bestimmt.

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ANALYSIS OF PERMANENT GASES BY GAS–SOLID CHROMATOGRAPHY USING AN IONISATION METHOD FOR DETECTION

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INTRODUCTION

Investigational work on the gases obtained by the thermal treatment of experimental ceramic fuel-element pellets required an analytical technique which would enable very small samples of permanent gases to be examined. KYRYACOS AND BOORD[1] used gas–solid chromatography on Linde Type 5A molecular sieve (a synthetic calcium zeolite) for the separation of hydrogen, oxygen, nitrogen, methane and carbon monoxide. Extending this technique, TIMMS, KONRATH AND CHIRNSIDE[2] attained a detection level of 0.5 μl of oxygen, approximately, using hydrogen as carrier gas and a conventional katharometer as detector. Using carefully purified helium as carrier gas, and employing a transistorised constant-voltage supply to an accurately thermostatically controlled katharometer, WILKINS AND WILSON[3] were able to detect 0.1 μl of oxygen.

LOVELOCK[4], in producing a supersensitive detector for many organic substances, used the property of argon atoms excited (but not ionised) by a radioactive source of ionisation to transfer their excitation energy to test substances and thus to ionise them. This produces a relatively large increase in the standing ionisation current in a detector cell. The permanent gases, however, have ionisation potentials greater than that of the excited state of argon (11.6 eV), and consequently yield no signal with the LOVELOCK detector. LOVELOCK has suggested that high-purity helium would be advantageous in this detector because of the much higher excitation potential of its metastable state. He considers, however, that commercial helium contains sufficient impurity to modify this effect by discharging excited helium atoms.

WILLIS[5] employed as carrier gas argon containing ethylene (1–100 p.p.m.) or acetylene, to detect small quantities of permanent gases by their diminution effects on a relatively high standing ionisation current carried by the impure argon. Detection of 1 p.p.m. of nitrogen is claimed, though the sample size is not defined.

The use of helium carrier gas with a LOVELOCK detector has been applied to the analysis of mixtures of hydrogen, oxygen, nitrogen, methane and carbon monoxide.

APPARATUS

The apparatus, shown diagrammatically in Fig. 1, consisted of a standard Pye Argon Chromatograph unit (W. G. Pye & Co., Cambridge) having a radium-*D* ionising source

in the detector, together with an appropriate glass gas-handling system, enabling carrier gas to flow through either sample volume or by-pass. The column comprised 4 ft × 0.25 in. i.d. glass tube within the heated jacket at 100° with a linkage to the sample system (1 ft × 0.25 in. i.d. glass) at room temperature; the whole of the

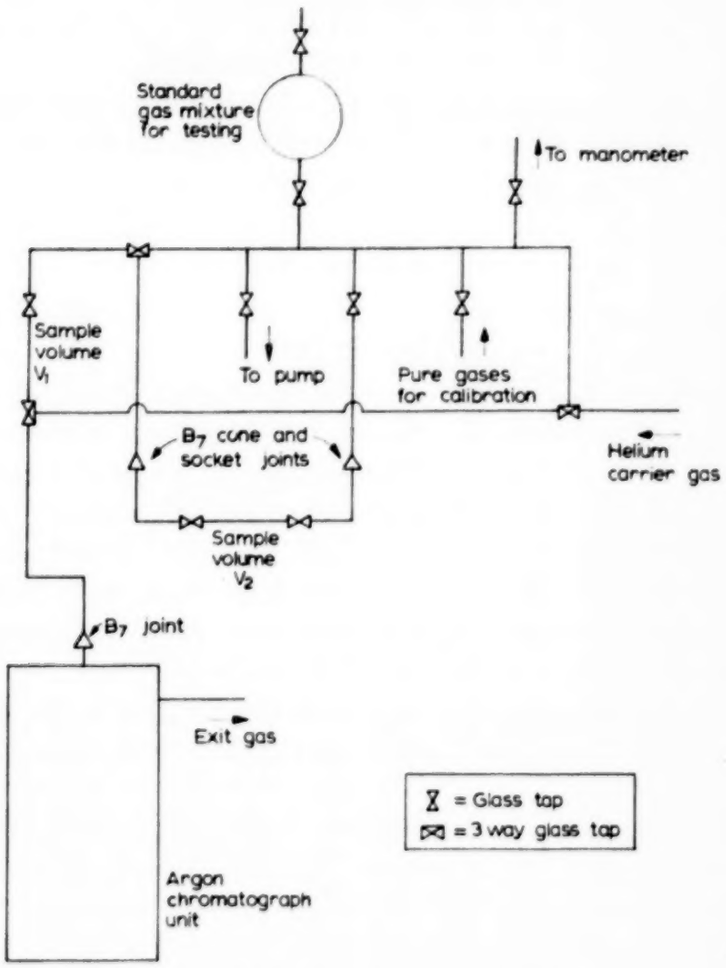

Fig. 1. Line diagram of apparatus.

5-ft length was packed with ground Linde molecular sieve type 5A sieved to 52–72 B.S. mesh and pre-activated by heating to 350–400° in air for one hour. A flow rate of 40 ml/min of helium was applied at a pressure drop of about 420 mm Hg across the column. The helium used was supplied by Airco Ltd., New Jersey, U.S.A., under specification of better than 99.7% purity. Before use it was passed through a column 5 ft × 0.5 in. i.d. containing Linde type 4A molecular sieves activated by heating to 350° *in vacuo* for one hour. This served to remove any traces of water vapour left in the helium.

DISCUSSION AND RESULTS

Nature of signal

When 750 V were applied across the detector cell the elution of sample gases from the column brought about only minute changes in ionisation current, these being in the negative sense, *i.e.* diminution. When the detector potential was increased to

1250 V, however, with consequent increase in the standing ionisation current, strong and repeatable negative signals were obtained during elution of hydrogen, oxygen, nitrogen, methane and carbon monoxide. This negative signal may be presumed to arise as a result of a combination of the following principal processes:

electrons (From ionising source energy $\geqslant E$)	+ He ——→	He* (Excited, metastable state)	+	electrons (Energy $< E$)	(1)
He*	+ foreign gas →	He	+	ionised foreign gas	(2)
electrons (from ionising source energy $\geqslant E$)	+ foreign gas →	electrons (Energy $< E$)	+	Energised but non-ionised foreign gas	(3)

It is inferred that most of the standing ionisation current is carried by inherent impurities in the commercial helium. After a settlement period (usually about 48 h) this becomes virtually constant for a given applied voltage. The standing ionisation current is produced by the consecutive processes (1) and (2), metastable helium acting as an intermediate in the ionisation process. When an excess of foreign gas appears in the detector, as in the case of an eluting component of a sample gas mixture, process (3) occurs to a large extent. Many electrons from the ionising-source lose energy by collision with foreign gas molecules without ionising them. These electrons have then insufficient energy to excite the helium atoms to the metastable state (process 1) and consequently the extent of the ionising process (2) is cut down. Thus during elution a negative signal is produced.

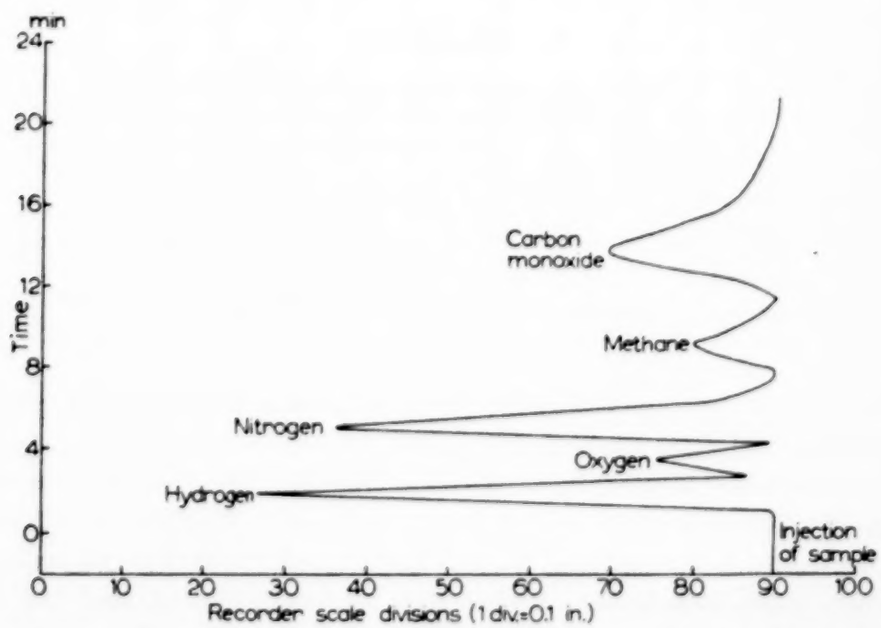

Fig. 2. Typical chromatogram. Sample size: 31.5 mm Hg pressure in 2 ml at 20°. Analysis: H_2 14.6; O_2 1.0; N_2 7.5; CH_4 2.6; CO 5.8 mm Hg. Total 31.5 mm Hg in 2 ml.

Calibration and operation

Elution times for various components are given in Table I, and a typical chromatogram of a synthetic mixture is shown in Fig. 2. Some typical calibration curves are shown in Fig. 3.

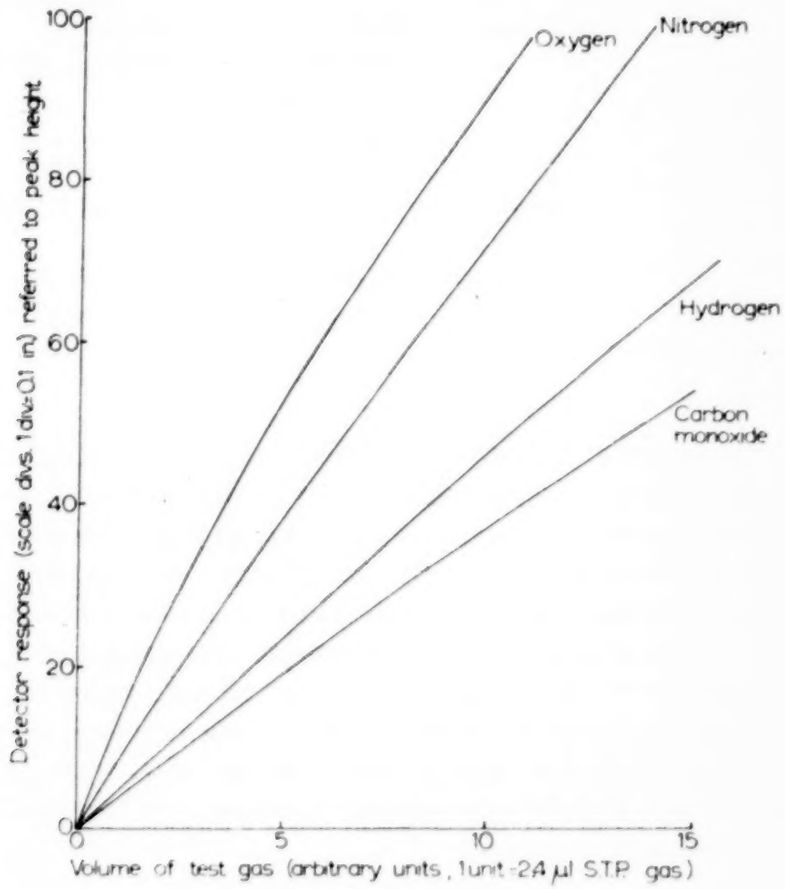

Fig. 3. Typical calibration curves.

TABLE 1

ELUTION TIMES FOR VARIOUS GASES

Gas	*Elution time referred to peak maximum*
Hydrogen	1 min 50 sec
Oxygen	3 min 25 sec
Nitrogen	5 min 0 sec
Methane	9 min 5 sec
Carbon monoxide	13 min 35 sec

The calibration curves based on peak height are non-linear, that for oxygen more so than the others. Calibration with somewhat larger samples with a reduced signal shows that at relatively large sample sizes ($>$ 100 µl s.t.p. gas) there is an increasing tendency for the response curve to level out. This may possibly be attributed to the increasing tendency of foreign gas at the higher concentrations to be ionised direct by the primary ionising radiation rather than through the excited state of helium. This process would work against the negative signal produced, as described in the previous sub-section.

The baseline is more sensitive to changes in flow rate than when the detector is used with argon as carrier gas, but variations of $\pm 5\%$ can be tolerated. After about 48 h settlement period from start-up, the calibration remains stable until at least 95% of the helium in the supply cylinder has been used up, always assuming that the column has been kept free from water which alters its elution characteristics. Both the fixed (V_1) and demountable (V_2) sample volumes (capacity 2 ml) have been used successfully. Fig. 3 represents conditions of normal use in this laboratory, though additional amplification enables an ultimate detection level of 0.1 μl s.t.p. gas to be attained. Only infrequent calibration checks are needed during operation, though recalibration is essential when the carrier gas supply cylinder is changed (approximately every two months).

CONCLUSION

The method described represents an adequate means of applying a LOVELOCK detector to the detection of permanent gases in gas–solid elution chromatography. Accuracies comparable with those of the best katharometers can be obtained.

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SUMMARY

A method is described for the analysis of hydrogen, oxygen, nitrogen, methane and carbon monoxide by gas–solid chromatography, using an ionisation method for detection. Accuracies of determination comparable with those of the best katharometers are attainable, without the need for the high accuracy of flow control or careful thermostatic control associated with katharometers. An ultimate detection level of 0.1 μl of s.t.p. gas can be obtained.

RÉSUMÉ

Une méthode est décrite pour l'analyse de l'hydrogène, de l'oxygène, de l'azote, du méthane et de l'oxyde de carbone par chromatographie gaz–solide, utilisant une méthode d'ionisation pour l'identification.

ZUSAMMENFASSUNG

Beschreibung einer gas–chromatographischen Methode zur Analyse von Gasgemischen, die Wasserstoff, Sauerstoff, Stickstoff, Methan und Kohlenmonoxyd enthalten. Zur Identifizierung wird eine Ionisationsmethode verwandt.

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ABSORPTION OF AMINES ON CATION EXCHANGE RESINS*

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That ion exchange resins can absorb uncharged molecules is well known. To some degree these resins can be regarded as organic solvents, capable of absorbing or "dissolving" organic and even inorganic compounds, sometimes in apparent defiance of Coulomb's law. An extreme example is the strong absorption of anionic complexes of Fe(III), Au(III) and Ga(III) by cation exchange resins from concentrated chloride solutions, presumably as ion pairs[1]. These metals are extracted from hydrochloric acid solutions by ether, and the solvent action of the resin may be analogous.

Many examples of non-ionic absorption by cation and anion exchange resins can be cited. Sugars[2,3], aldehydes[4], ketones[5], alcohols[6,7], carboxylic acids[7,8] and even hydrocarbons[7] can be bound. The absorptive action can be understood in terms of ion-dipole interactions and the attraction of benzene rings in polystyrene-type resins for aromatic rings of the absorbate.

These effects greatly strengthen the binding of organic anions and cations. The benzene sulfonate ion is very strongly bound by anion exchange resins of the polystyrene type, and the phenyl trimethyl ammonium cation is very strongly bound by this class of cation exchange resins. Complex ions of Ag(I) and benzylamine are decidedly more stable inside a sulfonated polystyrene cation exchange resin than in aqueous solution[9].

Ionic and non-ionic binding may occur together. If a solution of phenol in water is passed through a column of a polystyrene-type strong base anion exchanger, the resin absorbs nearly twice as much phenol as would be expected from the ion exchange capacity[10]. Neutral phenol molecules are absorbed as well as phenolate ions. The phenol bound in excess of the ion exchange capacity can be washed out of the resin with methanol; the rest must be displaced by ion exchange, for example by passing sodium hydroxide solution.

An even more striking example of absorption in excess of exchange capacity is the uptake of acetic acid by strong base anion exchanges from benzene solution. The total uptake is four times the exchange capacity[11].

The purpose of our investigation was to study the ionic and non-ionic binding of aromatic and aliphatic amines by cation exchange resins. Absorption over and above the ion exchange capacity was found in a few cases, and was found to depend greatly upon the solvent used. Distribution coefficients between resins and solutions were measured in four different solvents, and the possibilities of chromatographic separations were explored.

* Based on the Ph.D. thesis of S. R. WATKINS, University of Colorado, 1958.

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EXPERIMENTAL

Materials

Four cation exchange resins were used: Amberlite IR-120 and Amberlite IRC-50, both supplied by the Rohm and Haas Co.; Dowex 50WX4 and Dowex 50WX8, both supplied by the Dow Chemical Co. All the resins were in bead form. The Amberlite resins were 20–50 mesh; IRC-50 is a crosslinked polyacrylic acid, IR-120 a crosslinked sulfonated polystyrene. The Dowex resins were "white" grade sulfonated polystyrenes with 4% and 8% divinylbenzene crosslinking and were respectively 100–200 mesh and 50–100 mesh. All were thoroughly washed in the usual manner before use.

The amines used were aniline, benzylamine, pyridine, piperidine and *n*-butylamine. Reagent grade materials were distilled from quicklime or barium oxide before use.

The solvents used, besides water, were glacial acetic acid, methanol, ethanol, ispropanol and dioxane. Only the dioxane required special purification; it was refluxed with aqueous hydrochloric acid in a stream of nitrogen, dried with solid potassium hydroxide, and refluxed with metallic sodium before final distillation[12].

Analytical methods

The more strongly basic amines were determined by titration in aqueous solution with standard acid. Weakly basic amines (pyridine, aniline) were titrated in glacial acetic acid solution where this was convenient, using perchloric acid in glacial acetic acid as the titrant. Aniline, pyridine and benzylamine were also determined by ultraviolet absorption. Maximum absorption occurs close to 255 mμ in all cases, but the spectra between 240 and 270 mμ are sufficiently different that the three compounds can be distinguished. Measurements were made with Beckman Model DU and Cary Model 14 spectrophotometers. Aniline was also determined by a bromination method using standard solutions of potassium bromate and sodium thiosulfate; *n*-butylamine was determined colorimetrically with ninhydrin.

The ion exchange capacities of the resins were found by stirring the hydrogen resins with calcium chloride solution and titrating with standard base.

Static absorption studies

Weighed 3–4-g quantities of resins were placed in flasks with 100 ml of solutions of amines. For the experiments with dioxane as solvent the resins were first extracted with dioxane, then vacuum dried over phosphoric anhydride. For the other experiments, air-dried resins were used, containing some 20% of moisture. The flasks were closed and left to stand at 20°–25° for 1–3 weeks, shaking intermittently, until samples removed for analysis showed no further change with time. The amount of absorbed amines was calculated from the analysis of the solution, and in some cases also by extracting the amines from the resin by hydrochloric acid and determining the amine extracted.

Three sets of absorption studies were made. In the first, resins in the hydrogen form were shaken with solutions of amines in various solvents. In the second, resins containing sodium, calcium and magnesium ions as their exchangeable cations were shaken with solutions of amines. In the third, the resin Dowex 50WX8 in the hydrogen form was shaken with aqueous solutions of pyridinium chloride, with and without added hydrochloric acid, to determine the distribution ratio with pyridinium ions and hydronium ions between the resin and the solution.

Column absorption and elution studies

Resin columns 0.9 cm^2 in area and 16–26 cm high were used. Most work was done with 26-cm columns and flow rates of 1 ml/min. Where a solvent other than water was to be used, about one liter of this solvent was passed through the column before adding the sample.

In most of the experiments only one amine was put on the column at a time. Two groups of experiments were performed. In one, the resin column was saturated with aniline and pyridine, then eluted with methanol and dilute hydrochloric acid, to determine its capacity for non-ionic and ionic binding. In the other, small amounts (0.2–0.25 mmol) of amines were absorbed on the top of the columns, then eluted with hydrochloric acid in water, methanol, ethanol and isopropanol. The alcoholic solutions were prepared by passing hydrogen chloride gas into the anhydrous solvents. The main object of these experiments was to obtain distribution coefficients for the amine cations and hydrogen ions, and thereby to explore possibilities of chromatographic separations.

Experiments were then made to separate two pairs of amines, aniline from pyridine and aniline from benzylamine, by elution chromatography. Small quantities of the mixed amines were placed on the top of the column and eluted, the first pair with hydrochloric acid in absolute ethanol, the second with aqueous hydrochloric acid. Successful separations were accomplished.

RESULTS AND DISCUSSION

Static absorption studies

Figs. 1 and 2 show typical graphs of amine absorption against final concentration of dissolved amine. Similar graphs were obtained for other amines. They show that the amines are absorbed in excess of the ion exchange capacity when water is the solvent, but not when the solvent is methanol, acetic acid or dioxane. From dioxane containing 10% of water, aniline was absorbed up to the exchange capacity of the resin, but not beyond. The more carefully water was excluded, the less the amines were absorbed from dioxane. This fact is undoubtedly related to the very small swelling of the resins in anhydrous dioxane. Absence of swelling greatly reduces the rate of ion exchange, though it does not stop it[11], and it is almost certain that our data do not represent a true equilibrium.

The same is true to a lesser extent for absorption from glacial acetic acid. Air-dried resins, were used containing some 20% moisture, in the shaking tests with this solvent; had the solvent been truly anhydrous, the absorption of amines might have been considerably less. Swelling in glacial acetic acid is not zero, but it is very small; Dowex 50WX4 swelled only one-fifth as much in glacial acetic acid as it did in water.

The excess absorption from water solutions, over and above the exchange capacity, is summarized in Table I. Benzylamine is the most strongly absorbed as the neutral amine, then aniline, then pyridine. The resin with 4% crosslinking absorbed more amine than that with 8% crosslinking, and wide differences were found between the sulfonated polystyrene resins from the two manufacturers.

Fig. 3 gives absorption isotherms for uncharged aniline on the 4% crosslinked resin with four different exchangeable cations. The anilinium ion, understandably, gives the greatest absorption, followed by Mg^{+2}, Ca^{+2} and Na^{+}. For the inorganic cations the absorption increases with increasing charge: radius ratio.

Using the polyacrylic acid resin, Amberlite IRC-50, in the sodium form, no absorption of aniline was observed. This resin absorbed the more strongly basic amines from water up to its normal exchange capacity, but not beyond. In glacial acetic acid it swelled hardly at all and only absorbed a small amount of amines.

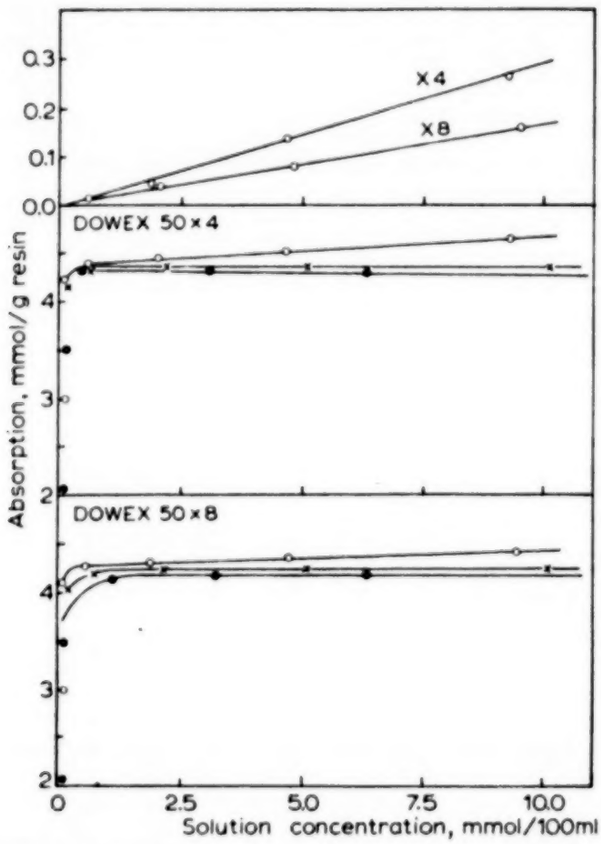

Fig. 1. Absorption of pyridine by sulfonated polystyrene resins. Absorption above capacity from water. Solvent: ○ water; ● acetic acid; × dioxane.

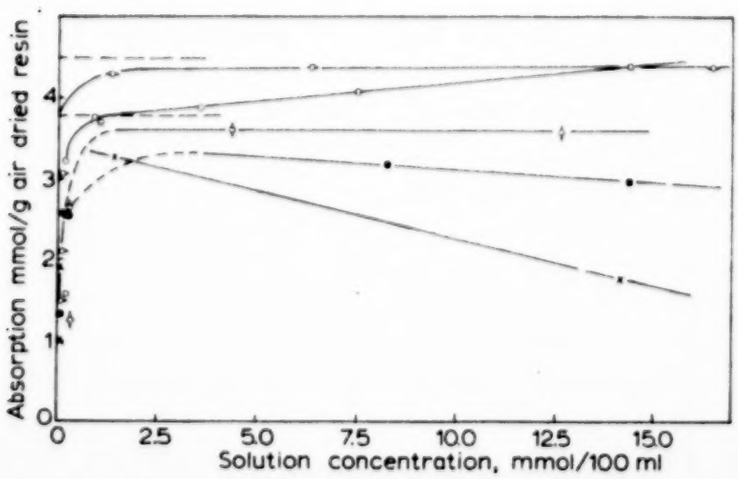

Fig. 2. Absorption of aniline by sulfonated polystyrene resins. All experiments except those with 90% dioxane were made with Amberlite IR-120 resin, capacity 3.80 mequiv./g; 90% dioxane experiments with resin of capacity 4.51 mequiv./g. Solvent: ○ water; ● acetic acid; ◇ methyl alcohol; × dioxane; ◈ 90% dioxane–10% water.

TABLE I

ABSORPTION ABOVE EXCHANGE CAPACITY

Amine	*Absorption, mmol/mequiv. resin*		*Amberlite IR-120*
	Dowex 50X4	*Dowex 50X8*	
Aniline	0.20	0.15	0.103
Benzylamine			0.131
Pyridine	0.068	0.040	0.042
n-Butylamine			0.029
Piperidine			0.029

Absorption is from 0.10 *M* aqueous amine solutions

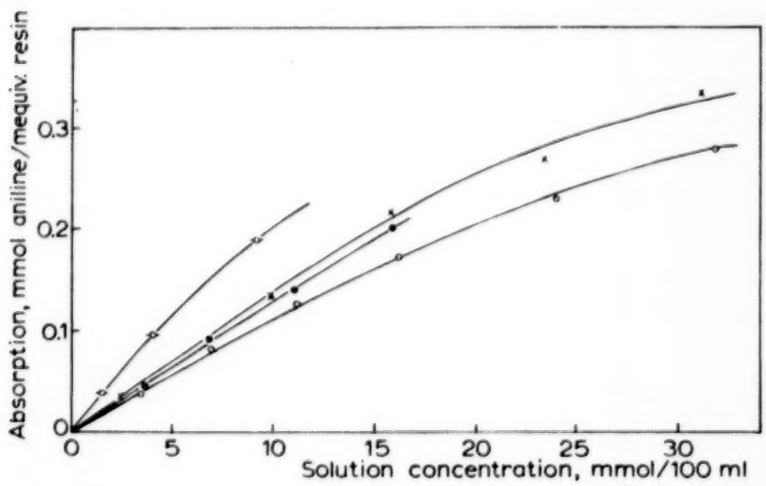

Fig. 3. Absorption of uncharged aniline on Dowex-50 resin, 4% crosslinked, with different exchangeable cations. Resin form: ⊖ anilinium; ○ sodium; ● calcium; × magnesium.

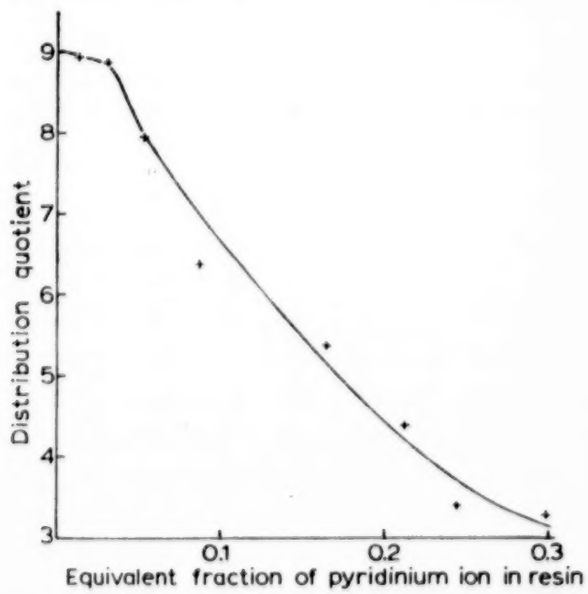

Fig. 4. Pyridinium ion–hydrogen ion exchange on 8% crosslinked resin at 25°.

The exchange isotherm for the pyridinium-hydrogen ion exchange on Dowex 50WX8 at 25° ± 2° is shown in Fig. 4. The quantity Q is the quotient:

$$\left(\frac{\text{moles pyridinium ion}}{\text{moles hydrogen ion}}\right)_{\text{resin}} \times \left(\frac{\text{moles hydrogen ion}}{\text{moles pyridinium ion}}\right)_{\text{water}}$$

The solution normality was 1.00. The distribution quotient shows the expected fall with increasing proportion of pyridinium ions in the resin, and its maximum value agrees well with the distribution quotient found in the column elution experiments.

Column elution studies

(*a*) *Saturation studies.* Here a column of Amberlite IR-120 in the hydrogen form was saturated with aniline by passing an aqueous 0.1-*M* solution. The exchange capacity of the column was 42.0 mequiv.; 48.7 mmol of aniline were absorbed. When the column was washed with 250 ml of methanol, 7.2 mmol were removed corresponding to the non-ionic absorption. Of this, 6.8 mmol were removed in the first 50 ml. Washing with 1.1 l of 0.5 *N* hydrochloric acid in water removed an additional 41.1 mmol of aniline.

A similar experiment was performed with pyridine. Within experimental error, no absorption was observed in excess of the exchange capacity, and all the pyridine was recovered by passing one liter of 0.5 *N* hydrochloric acid.

(*b*) *Elution studies with individual amines.* About 0.22 mmol of amine was absorbed on the top of the column, then eluted with hydrochloric acid. All of these experiments were made with Dowex 50WX8, 50–100 mesh. Figs. 5 and 6 show the curves with

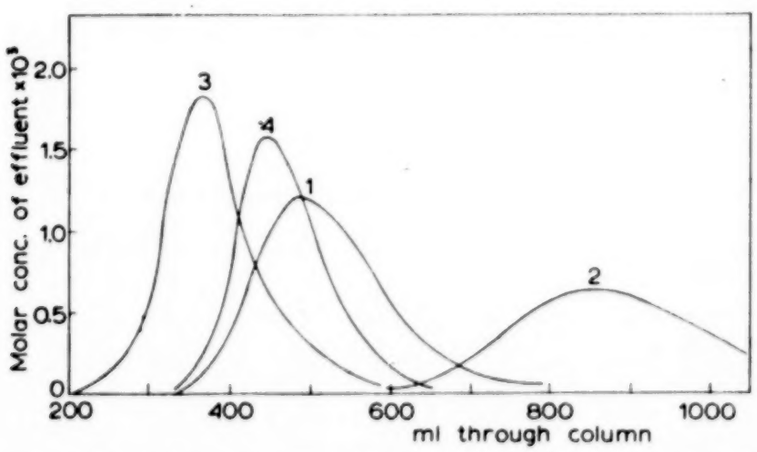

Fig. 5. Elution curves with 1 *N* HCl in water. Column: 24 ml bulk volume Dowex 50WX8. Loading: 0.22 mmol of each amine. 1–aniline; 2–benzylamine; 3–*n*-butylamine; 4–pyridine.

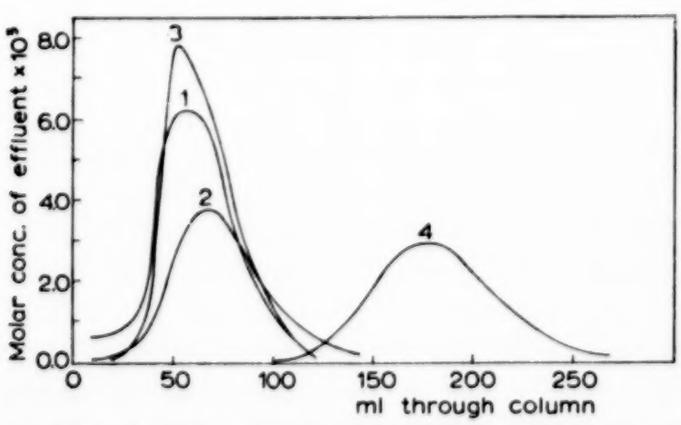

Fig. 6. Elution curves with 1 *N* HCl in methanol. Column: 22 ml bulk volume Dowex 50WX8. Loading: 0.22 mmol of each amine. 1–aniline; 2–benzylamine; 3–*n*-butylamine; 4–pyridine.

water and methanol as solvents; Tables II and III summarize the distribution coefficients calculated from the volumes of solution passed through the column at the peaks of the elution curves[13]. For these calculations the void fraction of the columns was taken to be 34%. This was an experimental value found by measuring the bulk volume occupied by a known weight of resin in the column and comparing it with the swollen bead volume found pyknometrically[14].

TABLE II

ELUTION DATA FOR AQUEOUS HCl SOLUTIONS

Amine	*HCl conc.*	*Resin*		*Volume to peak*	*C*	*D*
		Bulk vol.	*Void vol.*			
Aniline	1.00	24.3	8.3	485	60	43
	2.00	23.2	7.9	240	30	21
Benzylamine	1.00	24.3	8.3	850	102	74
	2.00	22.4	7.6	395	52	36
Pyridine	1.00	24.3	8.3	445	53	39
n-Butylamine	1.00	23.5	8.0	365	45	33

C = (base in resin)/(base in solution) in any given segment of the column; D = (moles base per g resin)/(moles base per ml solution)

TABLE III

ELUTION DATA FOR NONAQUEOUS SOLVENTS

Solvents	*Amine*	*For 1 M HCl*		*For 0.5 M HCl*	
		C	*D*	*C*	*D*
Methanol	Aniline	8.2	5.3		
	Benzylamine	9.3	6.0		
	Pyridine	25.4	16.3		
	n-Butylamine	7.6	4.9		
Ethanol	Aniline	6.4	4.2	15.3	10.0
	Benzylamine	11.6	7.8	22.2	14.5
	Pyridine	71	46.5		
	n-Butylamine	9.5	6.4		
Isopropanol	Aniline	4.8	3.2	9.5	6.4

For the meaning of C and D, see Table II

(*c*) *Separations.* From the elution data with single amines it appears possible to separate pyridine from the other amines by eluting with hydrochloric acid in alcohol, and benzylamine from the other amines by eluting with aqueous hydrochloric acid. Fig. 7 shows the separation of aniline from pyridine, which was clear-cut. The separation of aniline from benzylamine was less easy, but it was accomplished by using 4% crosslinked resin, 100–200 mesh, and a very slow flow rate; see Fig. 8. This clearly shows the importance of slow flow when exchanging large ions. In such cases the removal of the slow-moving ions from the resin proceeds even more slowly than their absorption, if a fastmoving ion like H^+ is being exchanged for them[15].

Examination of the curves in Figs. 5–8 will show that the recoveries of amines, estimated by integrating the elution curves, are incomplete in all cases except for the slowest flow (0.2 ml/min) in Fig. 8. In this case twice as much amine was used as in the other tests. Even here the aniline recovery is a little less, the benzylamine recovery a little more than 100%. The incomplete recovery can be attributed to

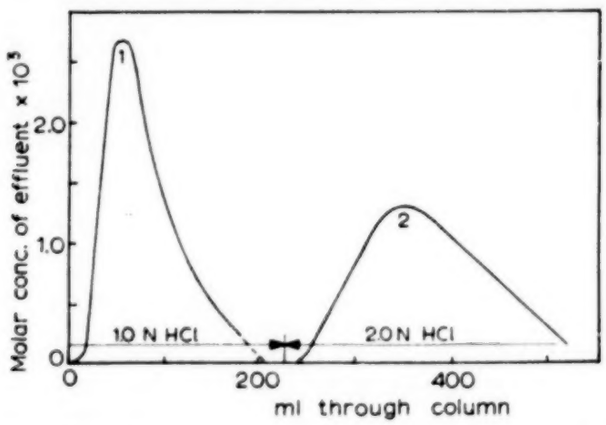

Fig. 7. Separation of aniline from pyridine. Column: 22 ml Dowex 50WX8. Loading: 0.22 mmol of each amine. Ethyl alcohol solvent. 1 – aniline; 2 – pyridine.

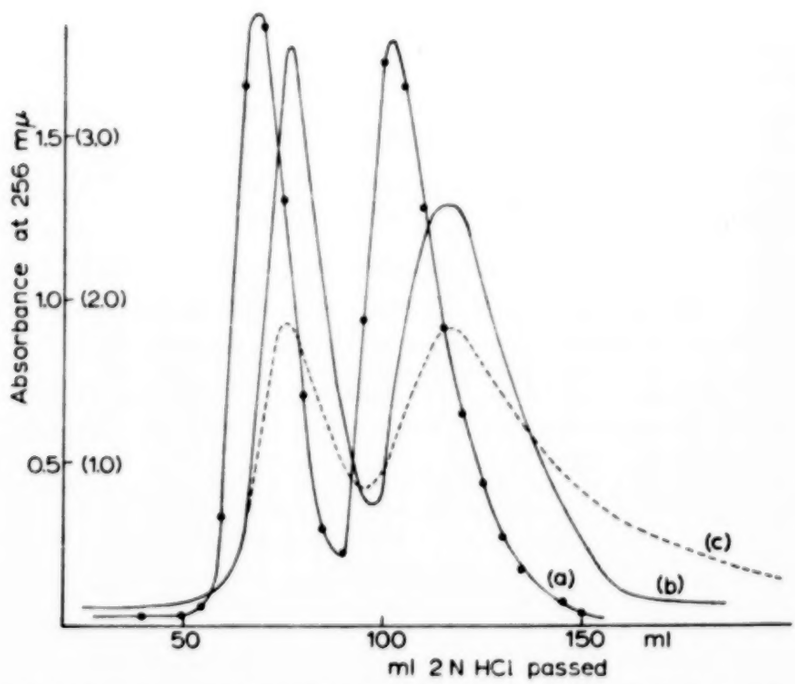

Fig. 8. Separation of aniline from benzylamine. Column: Dowex 50WX4, dry weight 2.8 g, bulk volume in 2 *N* HCl, 13.5 ml. Loading: 022 mmol aniline, 0.184 mmol benzylamine in runs (b) and (c); double these amounts in run (a). Flow rates: run (a) 0.2 ml/min; run (b) 1 ml/min; run (c) 3 ml/min. Molar absorbance at 256 mμ: aniline 133, benzylamine 189. Eluant: 2 *N* HCl in water.

insufficiently slow flow; one can visualize a certain fraction of the amines being held in the centres of the beads and not having time to diffuse out. Another cause of incomplete recovery, at any rate with aniline, is probably breakdown by air oxidation. The material in the "tail" beyond 150 ml in Fig. 8 was neither aniline nor benzyl-

amine; examination on the Cary recording spectrophotometer showed only a general absorption of light between 240 and 270 mμ with no band structure.

There was a very sharp change from the aniline spectrum to the benzylamine spectrum in passing the minima in the curves of Fig. 8 for the two slowest flow rates. Nevertheless it is hard to detect a few per cent of aniline in benzylamine from the ultra-violet spectrum alone.

ACKNOWLEDGEMENTS

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SUMMARY

All the amines studied are absorbed in excess of the exchange capacity by sulfonated polystyrene resins from aqueous solutions; the absorption is greatest with benzylamine, whose molecular structure is the closest to that of the monomer of the resin. The absorption is greater, the less the crosslinking of the resin, and it is influenced by the electrostatic field of the resin cations. There is no excess absorption from solvents such as alcohols, acetic acid or dioxane. The absorption characteristics of amines are sufficiently different that separations by elution chromatography on cation exchange resins are possible. Two such separations have been demonstrated. For quantitative analytical use, however, it would be wise to use very fine mesh resins on account of the slowness of diffusion of large amine molecules within the resins.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'absorption des amines sur des résines échangeurs de cations. Cette méthode permet une séparation de différentes amines.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Absorption von Aminen durch Ionenaustauscherharze. Die Methode ermöglicht eine Trennung verschiedener Amine.

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GAS–LIQUID CHROMATOGRAPHIC ANALYSIS OF AROMATIC HYDROCARBONS BOILING BETWEEN 202° AND 280° IN A LOW-TEMPERATURE COAL TAR*

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INTRODUCTION

In a previous publication[1] the Bureau of Mines reported the results of a detailed gas–liquid chromatographic analysis of aromatic hydrocarbons boiling up to 218° in a low-temperature bituminous coal tar. The present work extends this detailed characterization to include compounds boiling up to 280°, specifically, compounds in the range 202° to 280°.

Previously, only about 10 aromatic hydrocarbons boiling between 202° and 280°, including naphthalene and 5 alkylnaphthalenes, were found in low-temperature tars and in all instances by older techniques[2–6]. Quantitative results were essentially non-existent.

In the present work, employment of the eminently effective combination of gas–liquid chromatography and spectrophotometry enabled this laboratory to identify 48 compounds, including 9 mentioned in the previous publication. Of these identified compounds 20 are alkylnaphthalenes, including all isomeric dimethylnaphthalenes, except the 1,8-isomer. The rest of the compounds identified include methylated indans, tetralins, indenes and biphenyls, and some oxygenated aromatic hydrocarbons. Cyclohexylbenzene and 2a,3,4,5-tetrahydroacenaphthene, which had never been reported in any low-temperature tar, were also found. Quantitative determinations were made on nearly all compounds.

A correlation between logarithm of relative retention at 220° and boiling point for some alkylbenzenes and some alkylnaphthalenes was established; this made it possible to identify several additional constituents of the tar. This correlation is similar to the one for alkylbenzenes at 150°[1].

EXPERIMENTAL WORK AND RESULTS

Preparation of aromatic concentrates from the coal tar for gas–liquid chromatography

The same neutral oil from a West Virginia bituminous coal tar that was used in the earlier part of this work was used for the present analysis. The neutral oil was

* Presented at the Symposium on Tar and Pitch from Coal at the American Chemical Society meeting in New York, N.Y., September, 1960.

distilled to the equivalent of 260° in a Podbielniak Hyper-Cal high-temperature automatic distillation apparatus at 50 mm, with the results shown in Table I of the previous publication. The residue left from this distillation was further fractionated at 10 mm in a Fisher Unitized distillation apparatus with a 12-mm I.D. column, using a reflux ratio of 20 to 1. The results of this distillation are given in Table I.

TABLE I

FRACTION OF NEUTRAL OILS IN FISHER STILL

Charge:	8.35 wt.% of the tar	
	338.0 g	
Distillate:	131.4 g	= 38.9%
Residue:	201.8 g	= 59.7%
Loss and holdup:	4.8 g	= 1.4%

Fraction No.	*Head temperature, °C, (10 mm)*	*Estimated b.p. °C, (760 mm)*	*Weight g*
1	122–124	257–259	2.9
2	124–127	259–262	9.0
3	127–129	262–265	9.0
4	129–132	265–268	9.3
5	132–134	268–270	8.5
6	134–135	270–272	6.2
7	135–137	272–274	9.2
8	137–138	274–275	9.6
9	138–139	275–276	9.0
10	139–141	276–278	9.0
11	141–143	278–280	8.6
12	143–144	280–282	9.4
13	144–146	282–284	9.2
14	146–148	284–286	9.3
15	148–149	286–287	9.6
16	149	287	3.6
		Total	131.4

Equivalent atmospheric boiling points were estimated from a standard nomograph.

The distillate fractions were each separated into saturates, unsaturates, and aromatics by means of displacement chromatography with silica, as previously described. The data on displacement chromatography are summarized in Table II.

Analysis of aromatic hydrocarbons by gas–liquid chromatography (GLC)

Apparatus and operating conditions. A Perkin-Elmer model 154C Vapor Fractometer equipped with thermistor detectors was used. The response range of the recorder was from 0 to 2.5 mV, and the chart speed varied from 4 to 20 inches per hour, depending on the retention times of the components. The peak areas on the chromatogram were measured with a planimeter.

Two columns were used, each made from a 20-ft. × 1/4-in. O.D. copper tubing filled with approximately 75 g of packing made of 25% Apiezon L grease on 30- to 60-mesh firebrick. One of the columns was used at 200°, which was the temperature chosen for the analysis of the fractions boiling between 202° and 233°. The other column was

TABLE II

DISPLACEMENT CHROMATOGRAPHIC SEPARATION OF NEUTRAL OIL DISTILLATE FRACTIONS INTO CHEMICAL TYPES

Distillate fraction No.[a]	Weight of charge g	Column temperature °C	Saturates + some olefins			Aromatics + some olefins and some O, S compounds			Material retained on column g	Weight of aromatics identified by GLC g
			n_D^{20} range	Total weight g	Number of fractions	n_D^{20} range	Total weight g	Number of fractions		
7 + 8[b]	21	70	1.4025–1.4894	9.98	22	1.4915–1.5058	9.03	11	1.99	5.828
9[b]	4.29	70	1.4281–1.4705	1.77	8	1.4995–1.5867	1.94	7	0.58	1.329
10 + 11[b]	14.93	room temp.	1.4383–1.4938	7.04	18	1.4985–1.5640	6.36	13	1.53	3.152
12 + 13[c]	12.58	room temp.	1.4321–1.4900	5.00	14	1.4990–1.5790	5.87	13	1.71	3.089
14[c]	11.16	room temp.	1.4285–1.4769	5.17	13	1.4991–1.5864	5.24	13	0.75	2.314
15[c]	15.15	room temp.	1.4294–1.4839	6.80	17	1.4971–1.5947	7.31	18	1.04	5.419
16[c]	13.90	room temp.	1.4400–1.4830	4.11	11	1.5027–1.6039	7.81	18	1.98	5.771
17[c]	12.70	room temp.	1.4442–1.4843	2.96	9	1.5031–1.6047	6.97	15	2.77	4.322
18[c]	10.61	room temp.	1.4478–1.5059	3.40	8	1.5331–1.6050	6.14	12	1.07	4.665
19[c]	15.90	room temp.	1.4378–1.4971	6.05	13	1.5083–1.6005	7.13	13	2.72	4.647
20[c]	12.20	70	1.4317–1.5050	5.12	13	1.5219–1.5951	5.06	11	2.02	3.672
21[c]	16.36	70	1.4361–1.5079	6.02	14	1.5179–1.5968	9.11	16	1.23	5.989
22[c]	17.75	70	1.4386–1.5087	5.17	14	1.5218–1.5989	11.22	22	1.36	8.048
23[c]	17.14	70	1.4462–1.4988	3.89	9	1.5283–1.5916	12.24	20	1.01	8.516
24[c]	5.45	70	1.4480–1.5044	1.53	6	1.5449–1.5953	3.52	10	0.40	2.863
25[d]	16.42	85	1.4375–1.4769	2.20	6	1.5115–1.5970	12.73	23	1.49	11.502
26[d]	17.48	85	1.4395–1.4941	2.36	6	1.5228–1.5983	13.50	28	1.62	11.874
27[d]	17.55	85	1.4390–1.5000	2.25	6	1.5195–1.6014	13.59	23	1.71	10.691
28[d]	19.23	90	1.4349–1.4857	2.96	7	1.5100–1.6025	14.58	25	1.69	10.057
29[d]	10.19	90	1.4375–1.4941	2.03	5	1.5251–1.6040	7.00	12	1.16	5.414
1*[d]	2.90	95	1.4698	0.40	1	1.5489–1.6015	2.30	6	0.20	1.436
2*[d]	7.88	95	1.4572–1.4743	0.93	2	1.5359–1.6027	5.98	11	0.97	4.991
3*[d]	5.96	95	1.4509–1.4888	1.42	3	1.5421–1.5998	3.76	7	0.78	2.931
4*[d]	7.66	95	1.4537–1.5048	2.01	4	1.5232–1.5978	4.84	8	0.81	2.870
5*[d]	8.33	95	1.4591–1.4916	1.13	3	1.5172–1.5960	6.17	11	1.03	3.739
6*[d]	6.00	95	1.4587–1.4895	1.40	3	1.5189–1.5903	3.93	6	0.67	2.865
7*[d]	5.99	95	1.4555–1.5136	1.64	4	1.5460–1.6009	3.88	8	0.47	2.773
8*[d]	8.74	95	1.4565–1.5171	1.66	4	1.5340–1.5982	6.07	12	1.01	3.622

[a] Asterisk (*) designates fractions shown in Table I of this report; other fractions are shown in Table I of the previous report[1].
[b] Desorbent = butyl alcohol; [c] Desorbent = isobutyl alcohol; [d] Desorbent = cyclohexanol.

used at 220°, which was the temperature for the analysis of the fractions boiling between 233° and 275°. The samples varied in size from 5 μl to 15 μl and were injected into the column with a 50-μl syringe. The carrier gas was helium, admitted to the column at a pressure of 30 lb./in.^{2}, corresponding to a flow rate of 100 ml/min; the outlet pressure was atmospheric. The potential for the detector was 8 V. Throughout the work the temperature stayed within $\pm$ 0.1° and the helium pressure and the voltage of the detector stayed constant.

The efficiency of the column was calculated by using the equation[7]: No. of theoretical plates = $16(x/y)^2$, where y = length of peak baseline (as defined) and x = length from start of the run to middle of baseline section. Referring to 1,3,5-triethylbenzene and to 1-methylnaphthalene, the efficiency of the column at 200° was 2393 and 3948 theoretical plates, respectively, and for the column at 220° was 3364 and 4356.

General approach for identification. The retention times of 58 aromatic hydrocarbons boiling in the range of the neutral oil samples were obtained. Their calculated relative retentions (either time or volume) referred to 1,3,5-triethylbenzene at 200° and 220°, and their boiling points are shown in Table III. The aromatic fractions obtained by displacement chromatography were each examined by GLC under the same conditions as for the known compounds.

TABLE III

BOILING POINTS, RELATIVE RETENTIONS, AND CALIBRATION FACTORS (f_c) OF SOME AROMATIC HYDROCARBONS

Compound	*Boiling point*		*At 200°*		*At 220°*	
	°C (760 mm)	*Source*	*Relative retention*[a]	f_c[b]	*Relative retention*[a]	f_c[b]
n-Propylbenzene	159.217	e	0.86	0.37	0.40	0.85
1-Methyl-2-*n*-propylbenzene	184.80	e	0.62	0.95	0.64	0.93
1,4-Diethylbenzene	183.752	e	0.58	0.93	0.61	0.93
1,3-Dimethyl-5-ethylbenzene	183.75	e	0.58	0.91	0.60	0.89
1,2-Dimethyl-4-ethylbenzene	189.75	e	0.67	0.94	0.70	0.92
1-Methyl-3,5-diethylbenzene	200.70	e	0.77	1.00	0.79	0.97
1,2,4,5-Tetramethylbenzene	196.80	e	0.82	0.98	0.84	0.98
1,2,3,5-Tetramethylbenzene	198.00	e	0.85	1.02	0.87	0.99
1,3,5-Triethylbenzene	216.2	e	1.00	1.00	1.00	1.00
Pentamethylbenzene	231.8	e	1.72	1.01	1.75	1.00
Hexamethylbenzene	263.8	d	3.58	1.01	3.47	1.01
Cyclohexylbenzene	240.13	e	2.09	1.03	2.05	1.02
1,2,3,4-Tetrahydronaphthalene	207.57	e	1.14	1.54	1.16	1.52
Indan	177.82	e	0.59	1.42	—	—
Naphthalene	217.96	e	1.35	1.02	1.37	1.03
2-Methylnaphthalene	241.14	f	2.12	1.04	2.10	1.02
1-Methylnaphthalene	244.78	f	2.32	1.01	2.28	1.02
2-Ethylnaphthalene	257.9	e	3.01	1.08	2.93	1.07
1-Ethylnaphthalene	258.67	e	3.04	1.05	2.96	1.05
2,7-Dimethylnaphthalene	262	e	3.21	1.07	3.13	1.05
2,6-Dimethylnaphthalene	261	f	3.28	1.03	3.17	1.04
1,7-Dimethylnaphthalene	262.9	e	3.41	1.03	3.29	1.03
1,6-Dimethylnaphthalene	265.5	e	3.54	1.04	3.43	1.02
1,3-Dimethylnaphthalene	265	e	—	—	3.43	—
2,3-Dimethylnaphthalene	268	f	3.80	1.05	3.68	1.03

TABLE III (Continued)

Compound	Boiling point		At 200°		At 220°	
	°C (760 mm)	Source	Relative retention[a]	f_c[b]	Relative retention[a]	f_c[b]
1,5-Dimethylnaphthalene	270.1	e	3.99	1.03	3.83	1.03
1,2-Dimethylnaphthalene	271.1	g	4.10	—	3.93	—
1,3,7-Trimethylnaphthalene	281.7	e	—	—	4.88	1.09
2,3,6-Trimethylnapthalene	288.1	g	—	—	5.51	1.09
2,3,5-Trimethylnaphthalene	289	e	—	—	5.66	1.07
2a,3,4,5-Tetrahydroacenaphthene	252	e	2.88	1.20	2.80	1.20
Acenaphthalene	270	d	—	—	4.05	—
Acenaphthene	277.2	f	—	—	4.53	1.12
Biphenyl	255.0	e	2.66	1.01	2.60	1.00
3-Methylbiphenyl	272.70	e	—	—	3.82	1.04
2-Methylbiphenyl	260	d	2.46	—	2.51	1.06
4-Methylbiphenyl	267	d	—	—	3.10	—
2-Methylindene	204.1	e	1.05	1.08	1.08	1.06
2-Ethylindene	222.5	e	1.64	1.10	1.63	1.09
3-Ethylindene	218.1	e	1.58	1.08	1.57	1.09
1,3-Dimethylindene	207.5	e	1.09	—	1.10	—
2,3-Dimethylindene	224.5	e	1.70	—	1.69	—
2,6-Dimethylindene	226.8	e	1.63	1.09	1.62	1.07
1-Methyl-3-ethylindene	64–5 (1.3 mm)	e	1.62	—	1.60	—
3-Methyl-2-ethylindene	74–6 (1.25 mm)	e	2.40	—	2.34	—
2,3,6-Trimethylindene	242.6	e	2.57	—	2.51	—
Benzofuran	171.38	f	0.52	0.99	0.55	1.02
Dibenzofuran	287	f	—	—	5.02	1.18
Diphenyl ether	258.14	e	2.53	1.06	2.47	1.05
5-Methylindan	202.0	c	0.97[h]	—	0.96[h]	—
4-Methylindan	205.5	c	1.05[h]	—	1.07[h]	—
3-Methylindene	205	c	1.07[h]	—	1.09[h]	—
1,2,3,4-Tetramethylbenzene	205.04	c	1.01[h]	—	1.07[h]	—
1,6-Dimethylindan	210.9 (740.0 mm)	i	1.09[h]	—	1.07[h]	—
4,7-Dimethylindan	227.6 (745.5 mm)	j	1.67[h]	—	1.64[h]	—
2-Methyl-1,2,3,4-tetrahydronaphthalene	220.2	k	1.38[h]	—	1.35[h]	—
6-Methyl-1,2,3,4-tetrahydronaphthalene	229.03	c	1.75[h]	—	1.72[h]	—
1,4-Dimethylnaphthalene	268.5	c	—	—	3.70[h]	—

[a] Dead volume corrected.
[b] Defined in eqn. (1).
[c] API Research Project 44, *Selected Values of Properties of Hydrocarbons and Related Compounds*, Carnegie Institute of Technology, Pittsburgh, Pa.
[d] G. EGLOFF, *Physical Constants of Hydrocarbons*, Reinhold, New York, 1957.
[e] Determined in this laboratory.
[f] From Coal Tar Research Assoc., *Coal Tar Data Book*, Gomersal, near Leeds, Great Britain, 1953.
[g] From Gesellschaft für Teerverwertung mbH, *Gft-Aromaten*, Duisburg-Meiderich, Germany.
[h] The relative retentions of these compounds were determined from tar components identified by I.R.
[i] J. ENTEL, C. H. RUOF AND H. C. HOWARD, *Anal. Chem.*, 25 (1953) 1303.
[j] J. ENTEL, *Anal. Chem.*, 26 (1954) 612.
[k] A. S. BAILEY AND C. M. STAVELEY, *J. Inst. Petrol.*, 42 (1956) 97.

The approach for identification was principally the same as that described in the previous paper, except that ultraviolet spectrophotometry was included in addition to infrared. Components producing peaks were collected in the previously described manner. The ultraviolet spectra were obtained in cyclohexane solutions.

Generally, two methods were followed to identify the aromatic hydrocarbons. The first consisted of (*a*) preliminary identification of the unknown by comparing its retention time with those of known compounds, and (*b*) final confirmation of the identity by comparing the infrared spectrum of the collected material with that of the authentic specimen. In some instances, two components were found to have been eluted together. The infrared spectrum of the material producing a single peak served not only for qualitative identification but also for quantitative estimation of the components. The chromatograms for two different aromatic cuts shown in Fig. 1

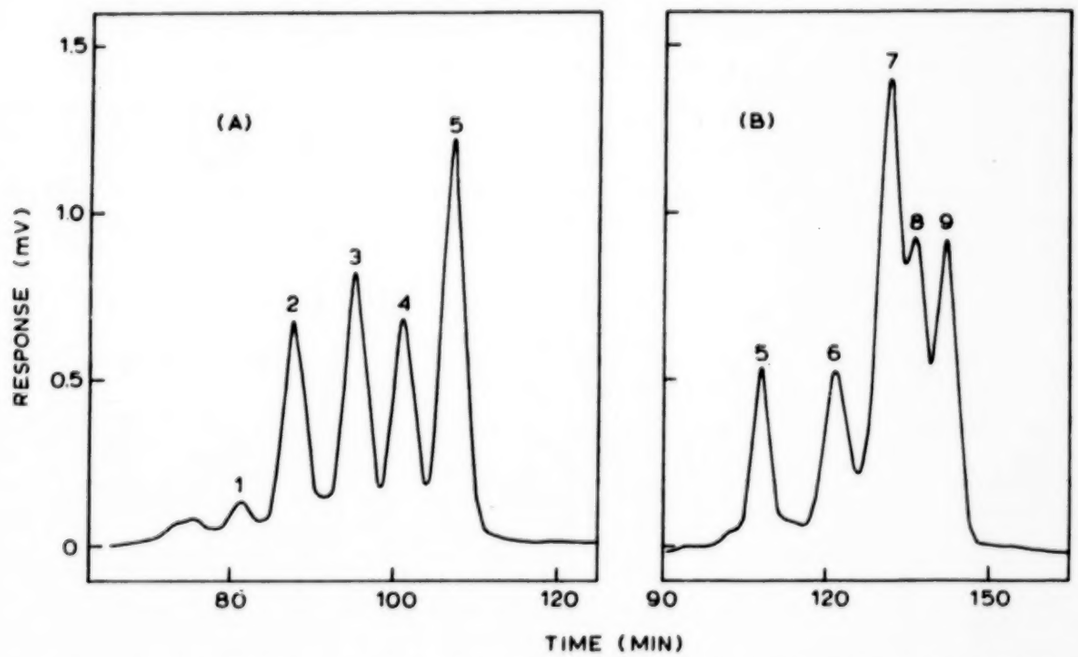

Fig. 1. Chromatograms of two aromatic cuts obtained from distillate fractions 10 + 11 (A) and 26 (B).

TABLE IV

IDENTIFICATION OF COMPONENTS PRODUCING ELUTION PEAKS IN THE GLC OF TWO AROMATIC CUTS FROM DISTILLATE FRACTIONS 10 + 11 AND 26

Peak No.	*Relative retention at 220°*	*Compound identified by I.R.*	*Relative retention of authentic specimen at 220°*
1	1.98	Not identified	—
2	2.08	2-Methylnaphthalene	2.10
3	2.29	1-Methylnaphthalene	2.28
4	2.47	Diphenyl ether	2.47
5	2.56	Biphenyl	2.60
6	2.91	2-Ethylnaphthalene	2.93
7	3.18	2,7-Dimethylnaphthalene	3.13
		2,6-Dimethylnaphthalene	3.17
8	3.30	1,7-Dimethylnaphthalene	3.29
9	3.46	1,3-Dimethylnaphthalene	3.43
		1,6-Dimethylnaphthalene	3.43

illustrate a good separation in (A) and a complete overlapping of some components in (B), which were subsequently identified and their ratios estimated by infrared spectrophotometry. Table IV shows the results of the identifications, the peak numbers in this table corresponding to the peak numbers in Fig. 1.

The second method of identification involved the correlation curves of relative retention and boiling points, which were applied in those instances where retention times of authentic specimens were not available. These correlation curves are shown in Fig. 2 and are discussed more fully in a later section. Boiling points of the components producing various peaks were obtained from their relative retention by these curves and were used as a preliminary means of identification. Since relative retention

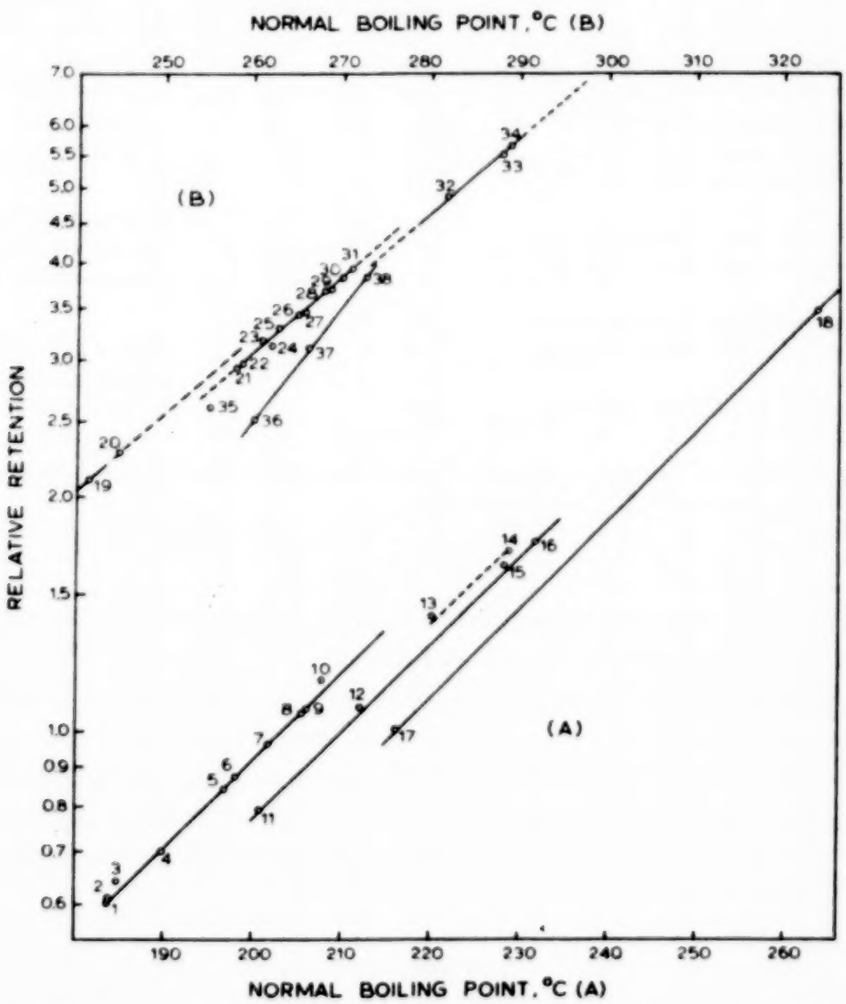

Fig. 2. Correlation between relative retentions and boiling points of some alkylbenzenes (A) and alkylnaphthalenes (B) at 220° on Apiezon L grease. (1) 1,3-Dimethyl-5-ethylbenzene; (2) 1,4-Diethylbenzene; (3) 1-Methyl-2-*n*-propylbenzene; (4) 1,2-Dimethyl-4-ethylbenzene; (5) 1,2,4,5-Tetramethylbenzene; (6) 1,2,3,5-Tetramethylbenzene; (7) 5-methylindan; (8) 4-Methylindan; (9) 1,2,3,4-Tetramethylbenzene; (10) 1,2,3,4-Tetrahydronaphthalene; (11) 1-Methyl-3,5-diethylbenzene; (12) 1,6-Dimethyl indan; (13) 2-Methyl-1,2,3,4-tetrahydronaphthalene; (14) 6-Methyl-1,2,3,4-tetrahydronaphthalene; (15) 4,7-Dimethyl indan; (16) Pentamethylbenzene; (17) 1,3,5-Triethylbenzene; (18) Hexamethylbenzene; (19) 2-Methylnaphthalene; (20) 1-Methylnaphthalene; (21) 2-Ethylnaphthalene; (22) 1-Ethylnaphthalene; (23) 2,6-Dimethylnaphthalene; (24) 2,7-Dimethylnaphthalene; (25) 1,7-Dimethylnaphthalene; (26) 1,3-Dimethylnaphthalene; (27) 1,6-Dimethylnaphthalene; (28) 2,3-Dimethylnaphthalene; (29) 1,4-Dimethylnaphthalene; (30) 1,5-Dimethylnaphthalene; (31) 1,2-Dimethylnaphthalene; (32) 1,3,7-Trimethylnaphthalene; (33) 2,3,6-Trimethylnaphthalene; (34) 2,3,5-Trimethylnaphthalene; (35) Biphenyl; (36) 2-Methylbiphenyl; (37) 4-Methylbiphenyl; (38) 3-Methylbiphenyl.

or boiling point could not be depended on entirely for identification, confirmation of identity depended on the comparison of the infrared or ultraviolet spectra of the collected samples with published spectra of the pure compounds. However, not all of the spectra of the probable constituents could be found in the literature; to substantiate the preliminary identification, spectral–structural correlations became

TABLE V

IDENTIFICATION OF EIGHT ALKYLNAPHTHALENES

Relative retention at 220°	*Compound*	*Literature[a] b.p., °C (760 mm)*	*B.p., °C obtained from the correlation curve*	*Spectroscopic identification*
3.70	1,4-Dimethylnaphthalene	268.5	268.4	Infrared
4.80	1,3,6-Trimethylnaphthalene	280	281.5	Ultraviolet
5.20	1,2,6-Trimethylnaphthalene	280	285	Ultraviolet
	1,2,7-Trimethylnaphthalene	278		Ultraviolet
4.39	1-Methyl-6-ethylnaphthalene, or 1-Ethyl-6-methylnaphthalene	273 / 270	277.3	Ultraviolet and infrared spectral–structural correlations
	1-Methyl-7-ethylnaphthalene, or 1-Ethyl-7-methylnaphthalene	271 / 270		
4.15	2-Methyl-6-ethylnaphthalene	270	275.2	Ultraviolet and infrared spectral–structural correlations
	2-Methyl-7-ethylnaphthalene	270		

[a] API Research Project 44, *Selected Values of Properties of Hydrocarbons and Related Compounds*, Carnegie Institute of Technology, Pittsburgh, Pa.

necessary. Table V shows eight alkylnaphthalenes identified by the second method. The details of these identifications are as follows:

(1) Constituent having a relative retention of 3.70: The boiling point of the constituent, obtained from its relative retention by the correlation curve for dimethylnaphthalenes, agreed very well with that of 1,4-dimethylnaphthalene. The identity of this naphthalene was confirmed by comparing the infrared spectrum of the constituent with that of 1,4-dimethylnaphthalene, published by the American Petroleum Institute (see Table VI).

TABLE VI

ANALYSIS OF INDIVIDUAL AROMATIC HYDROCARBONS BOILING BETWEEN 202° AND 280° IN NEUTRAL OIL DISTILLATE FRACTIONS

Compounds identified	*Fractions*	*Method of identification*	*Source of spectrum*	*Total weight g*	*Wt.% in neutral oil[a]*
1,2,3,4-Tetramethylbenzene[b]	6,7,8,9	Rel. retention–b.p. correlation, I.R.	[c]	1.0681	0.153
1,2-Dimethyl-3-*n*-propylbenzene[b]	5,6,7,8,9	Rel. retention–b.p. correlation, I.R.–structural correlation	–	0.2976	0.042

TABLE VI (Continued)

Compounds identified	*Fractions*	*Method of identification*	*Source of spectrum*	*Total weight g*	*Wt.% in neutral oil*[a]
1,4-Dimethyl-2-*n*-propylbenzene[b]	5,6,7,8,9	Rel. retention–b.p. correlation, I.R.–structural correlation	–	0.5874	0.084
1-Methyl-2,4-diethylbenzene[b]	6–13	Rel. retention–b.p. correlation, I.R.–structural correlation	–	0.9873	0.141
5-Methylindan[b]	5,6,7,8,9	Rel. retention–b.p. correlation, I.R.	[c]	1.7566	0.251
4-Methylindan[b,d]	5,6,7,8,9	Rel. retention–b.p. correlation, I.R.	[c]	1.7389	0.249
1,6-Dimethylindan	7–14	Rel. retention–b.p. correlation, I.R.	[c]	2.3746	0.340
4,7-Dimethylindan	7–16	Rel. retention–b.p. correlation, I.R.	[c]	1.3034	0.186
3-Methylindene[b]	5,6,7,8	I.R.	[c]	0.7141	0.102
3-Ethylindene	7–17	Rel. retention, I.R.	[e]	1.3126	0.188
2-Ethylindene	7–17	Rel. retention, I.R.	[e]	1.3032	0.186
2,3-Dimethylindene	7–17	Rel. retention, I.R.	[e]	1.7762	0.254
1,2,3,4-Tetrahydronaphthalene[b,d]	5,6,7,8	Rel. retention, I.R.	[e]	0.6170	0.088
2-Methyl-1,2,3,4-tetrahydronaphthalene	7–15	I.R.	[c]	1.0426	0.149
6-Methyl-1,2,3,4-tetrahydronaphthalene	12,13,14,15	I.R.	[c]	0.4958	0.071
Naphthalene[b,d]	6–15	Rel. retention, I.R.	[e]	6.3853	0.914
1-Methylnaphthalene[d]	14–24	Rel. retention, I.R.	[e]	12.0615	1.728
2-Methylnaphthalene[d]	12–24	Rel. retention, I.R.	[e]	16.1630	2.315
1-Ethylnaphthalene	20–29,1*[f]	Rel. retention, I.R.	[e]	1.9777	0.283
2-Ethylnaphthalene	20–29, 1*	Rel. retention, I.R.	[e]	3.1184	0.456
2,7-Dimethylnaphthalene	21–29,1*,2*	Rel. retention, I.R.	[e]	4.8187	0.690
1,7-Dimethylnaphthalene	23–29,1*,2*	Rel. retention, I.R.	[e]	4.7915	0.686
2,6-Dimethylnaphthalene[d]	23–29,1*,2*	Rel. retention, I.R.	[e]	4.1664	0.596
1,6-Dimethylnaphthalene[d]	25–29,1*–5*	Rel. retention, I.R.	[e]	6.4648	0.926
1,3-Dimethylnaphthalene	25–29,1*–5*	Rel. retention, I.R.	[e]	6.5617	0.940
2,3-Dimethylnaphthalene[d]	27,28,29, 1*–7*	Rel. retention, I.R.	[e]	3.8247	0.547
1,5-Dimethylnaphthalene	28,29, 1*–7*	Rel. retention, I.R.	[e]	3.6861	0.528

TABLE VI (Continued)

Compounds identified	*Fractions*	*Method of identification*	*Source of spectrum*	*Total weight g*	*Wt.% in neutral oil*[a]
1,2-Dimethylnaphthalene	29,1*–7*	Rel. retention, I.R.	[e]	3.5632	0.510
1,4-Dimethylnaphthalene	3*,4*	Rel. retention–b.p. correlation, I.R.	[e]	0.0979	0.014
2-Methyl-6-ethylnaphthalene / 2-Methyl-7-ethylnaphthalene	4*–8*	Rel. retention–b.p. correlation, U.V. and I.R.–structural correlations	–	3.9029	0.559
1-Methyl-7-ethylnaphthalene[g] and/or 1-Methyl-6-ethylnaphthalene[g]	4*–8*	Rel. retention–b.p. correlation, U.V. and I.R.–structural correlations	–	3.2925	0.471
1,3,6-Trimethylnaphthalene	5*–7*	Rel. retention–b.p. correlation, U.V.	[h]	0.7338	0.105
1,3,7-Trimethylnaphthalene	5*–7*	Rel. retention, I.R.	[e]	0.452	0.064
1,2,6-Trimethylnaphthalene / 1,2,7-Trimethylnaphthalene	6*–8*	Rel. retention–b.p. correlation, U.V.	[h] / [h]	0.8751	—
Biphenyl[d]	18–29,1*	Rel. retention, I.R.	[e]	18.8235	2.696
4-Methylbiphenyl	28,29,1*,2*	Rel. retention, I.R.	[e]	0.7271	0.104
3-Methylbiphenyl	1*–7*	Rel. retention, I.R.	[e]	1.2431	0.178
Cyclohexyl benzene	12–15	Rel. retention, I.R.	[e]	0.2769	0.039
2a,3,4,5-Tetrahydroacenaphthene	20–26	Rel. retention, I.R.	[e]	1.1713	0.167
Acenaphthylene	4*–6*	Rel. retention, I.R.	[e]	0.6963	0.099
Acenaphthene[d]	2*–8*	Rel. retention, I.R.	[e]	2.336	—
Diphenyl ether	18–29,1*,2*	Rel. retention, I.R.	[e]	38.5897	5.528
2,3-Dimethylbenzofuran	14–16	I.R.–structural correlation	–	0.1778	0.025
Dimethylbenzofuran II	7–13	I.R.–structural correlation	–	1.7848	0.255
Dimethylbenzofuran III	9–15	I.R.–structural correlation	–	0.6451	0.092
Dibenzofuran	5*–8*	Rel. retention, I.R.	[e]	1.4718	—

[a] Total neutral oil distilling up to about 360°, representing 16.92 wt.% of the total tar.
[b] Identified in prior work by this laboratory[1].
[c] American Petroleum Institute, Research Project 44, *Infrared spectral data*, Carnegie Institute of Technology, Pittsburgh, Pa.
[d] Previously identified by others[2–6].
[e] This laboratory.
[f] Asterisk (*) designates fractions shown in Table I of this report; other fractions are shown in Table I of the previous report[1].
[g] The positions of the ethyl and methyl groups might be reversed.
[h] E. HEILBRONNER, U. FRÖHLICHER AND P. A. PLATTNER, *Helv. Chim. Acta*, 32 (1949) 2479.

(2) Constituents having relative retentions of 4.80 and 5.20: According to the correlation curve for trimethylnaphthalenes, the boiling points for these constituents were 281.5° and 285°, respectively. They are somewhat higher than the literature values for 1,3,6-, 1,2,6-, and 1,2,7-trimethylnaphthalene. However, the ultraviolet spectrum of the sample having a relative retention of 4.80 matched well with the literature spectrum of 1,3,6-trimethylnaphthalene. The material having a relative retention of 5.20 was found to have more than one constituent and was collected as two individual samples, one corresponding to the first half of the peak and the other the second half. By comparing the ultraviolet spectra of the two samples with the published spectra of 1,2,6- and 1,2,7-trimethylnaphalene, the first sample was found to contain principally 1,2,6-, and the second to contain 1,2,7- as a major and 1,2,6- as a minor component.

(3) Constituents having a relative retention of 4.39: The boiling point obtained for this material from the trimethylnaphthalene correlation curve was 277.3°, a few degrees higher than any of the literature values for the four possible 1,6- and 1,7-methylethyl- and ethylmethylnaphthalenes. The identification of the material therefore depended mainly on spectral–structurel correlations, as follows: An examination of the ultraviolet spectra of 1-methyl, 1-ethyl-, 2-methyl-, and 2-ethylnaphthalene showed that the two 1-alkylnaphthalenes absorb at nearly identical maxima in the region of 300 mμ to 320 mμ but differ in absorptivities; the same is true for the two 2-alkylnaphthalenes. A similar situation was also observed in the 300 mμ to 330 mμ region for 1,4,5-trimethyl- and 1,4-dimethyl-5-ethylnaphthalene and for 1,3,5-trimethyl- and 1,3-dimethyl-5-ethylnaphthalene upon examining the ultraviolet spectral data of these compounds reported by EVANS, SMITH AND STRAUS[8]. This indicates that for absorption in the 300 mμ to 330 mμ region methyl groups and ethyl groups can be interchanged without significantly changing the position of the absorption peak; however, the absorptivities are usually altered. Therefore, naphthalene substituted with one methyl group and one ethyl group could be expected to show nearly identical absorption maxima in the 300 mμ to 330 mμ region as the naphthalenes substituted with two methyl groups *in the same positions*. The constituents had absorption bands at 307.8 mμ, 314.7 mμ and 322 mμ which are also exhibited by 1,6- and 1,7-dimethylnaphthalene, both of which had already been accounted for in much lower boiling fractions. It therefore appeared likely that one or more of the four possible 1,6- or 1,7-methylethyl- or ethylmethylnaphthalenes were present. The infrared spectrum of the material was in agreement with this conclusion. According to WERNER, KENNARD AND RAYSON[9], the two strong bands shown in the sample spectrum at 783 cm^{-1} and 810 cm^{-1} could be due to 3H and 2H out-of-plane deformation vibrations of 1,6-disubstituted naphthalene, and the other two strong bands at 760 cm^{-1} and 835 cm^{-1} could be due to the same vibrations of 1,7-disubstituted naphthalene.

(4) Constituents having a relative retention of 4.15: This material appeared to consist of a mixture of 2-methyl-6-ethyl- and 2-methyl-7-ethylnaphthalene. The boiling point of the sample found by the trimethylnaphthalene curve was several degrees higher than the literature value for the two naphthalenes. However, the ultraviolet absorption maxima in the 300–330 mμ range for the constituent producing the first half of the peak were at 303 mμ, 310 mμ, 317 mμ, and 324.8 mμ, in close agreement with the much lower boiling 2,6-dimethylnaphthalene. The maxima shown by the second constituent were nearly identical to those for 2,7-dimethylnaphthalene at 307 mμ, 317 mμ, and 321 mμ. The presence of 2-methyl-6-ethyl- and 2-methyl-7-

ethylnaphthalene was thus indicated. The infrared bands at 800 cm^{-1} to 900 cm^{-1} substantiated these identifications. The strong bands shown by the first constituent at 823 cm^{-1} and 874^{-1} and those shown by the second constituent at 835 cm^{-1} and 876 cm^{-1} could be due, respectively, to 2H and 1H out-of-plane deformation vibrations of 2,6- and 2,7-disubstituted naphthalenes[9].

In addition to these alkylnaphthalenes, three dialkylbenzofurans, of which one might be the 2,3-dimethyl-isomer, were tentatively identified by the characteristic infrared bands of benzofurans, observed by examining the spectra of benzofuran and all its monomethyl derivatives[10]. A strong band between 1,250 cm^{-1} and 1280 cm^{-1} and one or two between 1,090 cm^{-1} and 1,160 cm^{-1} could be characteristic of benzofurans. According to BELLAMY[11], compounds containing the structure =C—O— may absorb near 1,250 cm^{-1} and in unsaturated cyclic compounds, with the structure =C—O—C=, a band may appear near 1,100 cm^{-1} or somewhat higher frequencies. Therefore, in the spectra of the benzofuran constituents, the bands between 1,250 cm^{-1} and 1,280 cm^{-1} and between 1,090 cm^{-1} and 1,160 cm^{-1} may be due to the furan structure in the molecule.

One benzofuran sample, having a relative retention of 1.28 at 200°, showed a strong band at 1,251 cm^{-1} as in 2-methylbenzofuran and another strong band at 1,092 cm^{-1} as in 3-methylbenzofuran. This sample also absorbed strongly at 742 cm^{-1}, similarly to 2-methyl- and 3-methylbenzofuran, both of which have a band at 746 cm^{-1} that is probably due to the 4H out-of-plane deformation vibration in the benzene ring. The boiling point of 2,3-dimethylbenzofuran from the literature[12] is approximately 220°, which falls in the boiling range of the distillate fractions containing this component. It is, therefore, very likely that this constituent is 2,3-dimethylbenzofuran. The other two samples showed the characteristic infrared bands of benzofurans in both regions. In addition, a few sharp bands also appeared between 1,000 cm^{-1} and 1,400 cm^{-1}. These were considered to be dimethylbenzofurans, all of the isomers of which boil well within the range 210° to 230°.

Quantitative estimation of aromatic hydrocarbons. The internal standard method, which was described in the previous paper[1], was employed for quantitative analysis of the samples, 1,2,3-triethylbenzene being selected as the standard. The equation used for the calculations is as follows:

$$f_c = A_s W_c / A_c W_s \qquad (1)$$

where f_c is the calibration factor, as defined, A_s and A_c are the areas for the standard and component in the mixture, and W_c and W_s are the weight-percentages of the compound and the standard. The f_c values for a number of aromatic hydrocarbons were determined at 200° and 220° and are given in Table III. No significant difference was found between the values for each compound at these two temperatures. These values were used to determine the weight-percentages of the constituents in the fractions. For those compounds present in the tar for which authentic specimens were not available, the f_c values of their isomers or of structurally similar compounds were used. For example, an average f_c of 1.03 for six dimethylnaphthalenes was used to calculate the amounts of the 1,2- and 1,4-dimethyl isomers, an average of 1.08 for three trimethylnaphthalenes was used for other trimethyl and methylethylnaphthalenes, the f_c value of 0.99 for 1,2,3,5-tetramethylbenzene was used for 1,2,3,4-tetramethyl benzene, the value of 1.42 for indan was used for all indan derivatives, the value of

1.52 for tetralin was used for the two methyltetralins, and 1.05, an average of the values for 2-methyl- and 3-methylbiphenyl, was used for 4-methylbiphenyl.

The aromatic hydrocarbons boiling between 202° and 280° found in the low-temperature bituminous tar and their quantities are presented in Table VI. The values of weight-percentages in neutral oil of the three highest boiling components are not entered, since they are also expected to be present in the next higher boiling fraction.

DISCUSSION

Correlation between relative retentions and boiling points of alkylbenzenes and alkylnaphthalenes

When the logarithms of relative retentions at 220° for alkylbenzenes and for alkylnaphthalenes, in either instance having an equal number of carbon atoms in the alkyl groups, were plotted against their boiling points, a straight line resulted. The relationship is similar to that established for a number of alkylbenzenes at 150°, as previously reported[1].

Fig. 2 (A) shows three parallel lines corresponding to alkylbenzenes having 4, 5, and 6 carbon atoms in the alkyl groups. Indans, which have a benzene nucleus with a 1,2-trimethylene-type alkylation, fall closely on the correlation curves for alkylbenzenes having the corresponding number of carbon atoms in alkyl groups. However, tetralin (point 10 in Fig. 2), which has a 1,2-tetramethylene-type alkylation, does not fit so closely to the line for C_{10}-alkylbenzenes, and its 2-methyl- and 6-methyl-derivatives (points 13 and 14) are well off the line for C_{11}-alkylbenzenes. However, a line drawn between points 13 and 14 is essentially parallel to the line for the C_{11}-alkylbenzenes. No clear-cut relationship can be established between the indans and the tetralins with this limited data for alkyltetralins. Fig. 2 (B) shows three parallel straight lines corresponding to alkylnaphthalenes having 1, 2, and 3 carbon atoms in the alkyl groups. A fourth line representing three monomethylbiphenyls (points 36, 37, and 38) is not parallel to the naphthalene lines.

A difference in slope can be observed among the three groups — benzenes, naphthalenes, and biphenyls. The slope of the benzenes is 0.0113, that of the naphthalenes is 0.0098, and that of the biphenyls is 0.0164.

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SUMMARY

Gas–liquid chromatography, coupled with infrared and ultraviolet spectrophotometry, was used to analyze aromatic hydrocarbons boiling between 202° and 280° in the neutral oil portion of a low-temperature bituminous coal tar. A total of 48 compounds was identified, of which 20 were alkylnaphthalenes. Of these compounds, nine had also been mentioned in a previous report. Quantitative determinations were made on nearly all of the components. The analysis, especially from a quantitative standpoint, is by far the most detailed one carried out to date for the alkylnaphthalene cut of a low-temperature coal tar. It was shown that alkylnaphthalenes with equal numbers of carbon atoms in their alkyl groups displayed a linear relationship between log relative retention and normal boiling point, a situation similar to that for the alkylbenzene series, and that the values for the C_{11}, C_{12} and C_{13} alkylnaphthalenes lie on three parallel lines. Examples of the utility of these correlations are given.

RÉSUMÉ

Les auteurs ont appliqué la chromatographie gaz–liquide, combinée à la spectrophotométrie dans l'infra-rouge et l'ultra-violet, à l'analyse d'hydrocarbures aromatiques de goudrons, à point d'ébullition compris entre 202 et 280°. On a pu identifier ainsi jusqu'à 48 constituants. Presque toutes ces substances ont pu être déterminées quantitativement.

ZUSAMMENFASSUNG

Beschreibung der Analyse eines aromatischer Kohlenwasserstoffes mit Siedepunkten zwischen 202°–280°C aus der Neutralölfraktion eines Niedertemperatur- Bitumenteeres durch Gaschromatographie in Verbindung mit IR und UV-Spektrophotometrie. Es konnten 48 verschiedene Verbindungen nachgewiesen und zum grössten Teil quantitativ bestimmt werden.

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CATION EXCHANGE BEHAVIOUR OF STRONTIUM ON DOWEX 50W-X8

SEPARATION FROM MIXTURES

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In continuation of ion exchange studies of important fission product elements[1,2] it was deemed worthwhile to investigate the ion exchange behaviour of strontium.

TOMPKINS, KHYM AND COHN[3] in the course of examination of fission-produced radioisotopes separated barium from strontium by elution with 5% citric acid at pH 5. Barium was less strongly complexed than strontium, hence strontium was eluted first. BOVY AND DUYCKAERTS[4] separated traces of strontium from barium by selective elution with EDTA at pH 10.5. Distribution coefficient measurements[5] between Dowex 2 and phosphoric acid solutions showed that strontium is weakly adsorbed at low acid concentrations. Strontium was also found to be poorly adsorbed on Dowex 2 from hydrochloric, nitric or sulphuric acid solutions[6]. The adsorption of calcium and stron-

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tium[7] on Zeo Karb-225 has been studied over the pH range 3 to 7. At pH 5.25 only strontium remained adsorbed in the presence of EDTA and was finally eluted with 3 *N* hydrochloric acid.

This paper describes systematic studies on the cation exchange behaviour of strontium on Dowex 50W-X8 (hydrogen form), following essentially the same programme as in the previous study of barium[1]. Strontium has been similarly separated from various cations.

APPARATUS AND REAGENTS

The apparatus was the same as before[1]. Strontium nitrate solution, about 5 mg/ml. About 8 g of strontium nitrate (E. MERCK) was dissolved in 500 ml of water. The solution was standardized gravimetrically as strontium sulphate[8] and volumetrically by titration with permanganate after precipitation as oxalate[8,9]. For quantitative precipitation of strontium oxalate the aqueous solution must be made at least 50% in alcohol. Dowex 50W-X8 (Dow Chemical Co., Midland, Mich., U.S.A.), 50–100 mesh (hydrogen form) cation exchange resin.

EXPERIMENTAL, RESULTS AND DISCUSSION

Ion exchange studies

A strontium nitrate solution containing 29.98 mg of strontium was used throughout. The procedure was identical with that followed for barium[1]. The ion exchange behaviour towards nitric acid, hydrochloric acid and sodium nitrate are shown schematically in Fig. 1. Table I shows that strontium can be quantitatively recovered by

TABLE I

BEHAVIOUR OF STRONTIUM TOWARDS VARIOUS ELUTING AGENTS

Strontium = 29.98 mg; resin = 11.644 g (oven-dried, 1.4 × 17.5 cm)

	Eluting agent (50-ml fraction)		*Strontium recovery %*				*Total strontium recovery %*	*Elution constant E*	*Bed distribution coefficient D = 1/E*
			I	*II*	*III*	*IV*			
1	HNO_3	1.5 *M*	0	0	15.9	52.5	68.4	0.149	6.667
	HNO_3	2 *M*	1.2	39.6	56.1	0.7	97.6	0.2559	3.846
	HNO_3	3 *M*	60.6	32.9	4.3	0	97.8	0.8804	1.136
	HNO_3	4 *M*	76.3	25.2	0	0	101.5	0.8804	1.136
2	HCl	1.5 *M*	0.7	1.1	7.9	43.0	52.7	—	—
	HCl	2 *M*	0.98	28.9	55.6	9.5	95.0	0.2559	3.846
	HCl	3 *M*	12.6	84.5	1.7	0.8	99.6	0.4845	2.083
	HCl	4 *M*	32.6	65.3	1.5	1.1	100.5	0.4845	2.083
3	NH_4Cl	2 *M*	3.3	11.6	60.9	8.1	83.9	0.2063	4.762
	NH_4Cl	3 *M*	12.5	66.3	20.8	3.5	103.1	0.3365	2.941
	NH_4Cl	4 *M*	16.6	74.9	4.9	2.5	98.9	0.3365	2.941
4	$NaNO_3$	2 *M*	3.3	55.4	41.7	4.5	104.9	0.3365	2.941
	$NaNO_3$	3 *M*	20.2	61.9	9.5	4.8	96.4	0.3365	2.941
5	CH_3COONH_4	2 *M*	0.6	60.6	27.8	2.3	91.3	0.3365	2.941
	CH_3COONH_4	4 *M*	64.7	27.3	5.1	1.5	98.6	0.8804	1.136
6	Citric acid 5% (pH 5.1)		1.5	54	29.5	2.1	87.1	0.3365	2.941

elution with 200 ml of nitric acid (2–4 *M*), hydrochloric acid (3–4 *M*), ammonium chloride (3.4 *M*), sodium nitrate (2–3 *M*), and ammonium acetate (2–4 *M*). On the

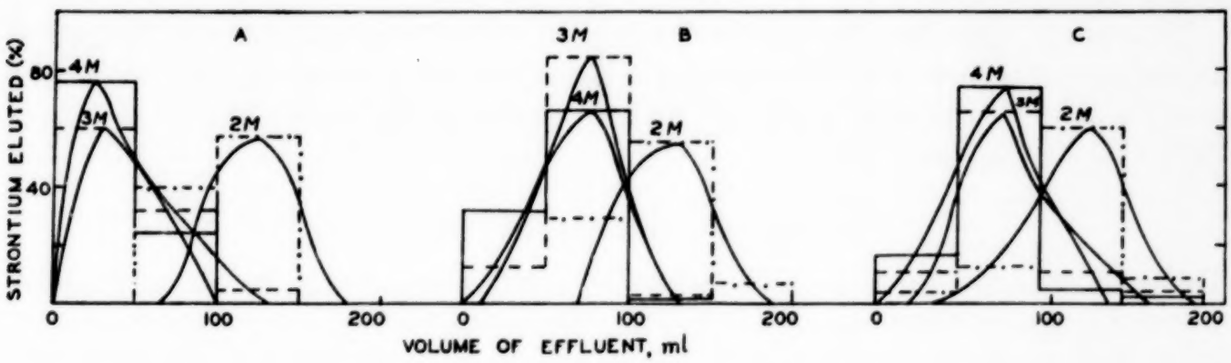

Fig. 1. Elution of strontium from Dowex 50W-X8: (A) HNO_3; (B) HCl; (C) NH_4Cl.

basis of the elution constants and bed distribution coefficients, the eluting agents can be arranged in order of decreasing efficiency: nitric acid > hydrochloric acid > sodium nitrate = ammonium chloride = ammonium acetate > citric acid.

The effluent fractions were assayed by the volumetric method (permanganate titration). In the case of acid eluants, the solution to be analysed was evaporated to dryness, but with salt eluants, the solution was used directly for analysis.

Ion exchange separations

Essentially the same principle was followed as in the case of barium for working out these separations. Thus strontium was separated from copper(II), mercury(II), caesium, zinc, cadmium and uranium(IV) by selective elution with 4 *M* hydrochloric acid. It was also separated from zirconium, thorium, iron(III) and bismuth with the help of suitable complexing agents such as citric acid and EDTA at proper pH. These separations are significant since most of the constituents in the synthetic mixtures represent important fission products.

The net operations in this method require about 4–5 h. The results are reproducible

TABLE II

ION EXCHANGE SEPARATIONS OF STRONTIUM

(Sr = 29.98 mg)

No.	*Foreign ion*	*Added mg*	*Strontium found, mg*	*Recovery %*
1	U(VI)	30	29.14	97.1
2	Cu(II)	32	30.3	101
3	Hg(II)	35	29.25	97.5
4	Cs(I)	31.2	29.77	99.3
5	Zn(II)	35	29.34	97.9
6	Cd(II)	25	31.20	104.0
7	Ag(I)[a]	35	29.93	96.5
8	Zr(IV)	28.5	28.72	95.8
9	Th(IV)	40	28.72	95.8
10	Fe(III)	31	29.5	98.4
11	Bi(III)	16.7	28.9	96.4

[a] Selective elution with 4 *M* HNO_3.

to within $\pm 3\%$. The ion exchange studies of calcium are in progress and will be reported soon.

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SUMMARY

The cation exchange chromatography of strontium on Dowex 50W-X8 is described. Nitric acid, hydrochloric acid, ammonium chloride, sodium nitrate, ammonium acetate and citric acid were examined as eluants. Strontium can be separated from important fission products such as caesium, zinc, cadmium, silver and zirconium and also from uranium(VI), thorium, bismuth, iron(III), copper(II) and mercury(II).

RÉSUMÉ

Les auteurs ont effectué une étude du comportement du strontium sur Dowex 50W-X8; cet élément a pu ainsi être séparé de produits de fission importants tels que: Cs, Zn, Cd, Ag et Zr, de même que de: U(VI), Th, Bi, Fe(III), Cu et Hg(II).

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das Verhalten von Strontium gegenüber dem Austauscherharz Dowex 50W-X8, bei Verwendung verschiedener Eluierungsmittel. Man kann unter geeigneten Bedingungen eine Trennung des Strontiums von anderen häufigen Spaltprodukten wie Cs, Zn, Cd, Ag, und Zr sowie auch von U(VI), Th, Bi, Fe(III), Cu und Hg(II) erzielen.

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THE COLORIMETRIC MICRO-DETERMINATION OF NICKEL AS TRIPHENYLMETHYLARSONIUM BIS-DITHIO-OXALATO NICKELATE(II)

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INTRODUCTION

The use of the triphenylmethylarsonium cation, in conjunction with an extractive technique, has already been examined for the colorimetric micro-determination of iron[1], copper[2] and cobalt[3], and in this paper the use of this cation, together with the reagent potassium dithio-oxalate, is suggested for the colorimetric determination of micro quantities of nickel.

The most widely used method for the colorimetric determination of nickel involves the addition of dimethylglyoxime to an ammoniacal nickel solution which has been treated with bromine or iodine[4-6]. The intensity of colour of the complex, however, increases rather rapidly with time[7]. The nickel may be separated from interfering ions by extraction of the nickel dimethylglyoxime complex into chloroform, but this yellow solution is too pale for direct measurement and the nickel must be re-extracted with dilute hydrochloric acid and determined in the aqueous solution after addition of dimethylglyoxime.

Other reagents which have been described for the colorimetric determination of nickel include 8-hydroxyquinoline[8], α-furildioxime[9,10], 4-methylcyclohexane-1,2-dione dioxime[11], quinoxaline-2,3-dithiol[12] and potassium dithio-oxalate[13,14]. The last reagent was prepared by JONES AND TASKER[15] in 1909 and was later used by FAIRHALL[13] to determine nickel with relatively high accuracy. YOE AND WIRSING[16] showed it to have greater sensitivity than other reagents, and used it to detect one part of nickel in 125 million parts of water.

The extractive method described in this paper gives a more stable test solution than that of the bis-dithio-oxalato nickelate(II) ion in water. Elimination of interferences is also simplified.

DISCUSSION

The stable red compound formed by the addition of triphenylmethylarsonium chloride and potassium dithio-oxalate solutions to a neutral or acid solution of the nickel(II) ion has been isolated, and can be extracted from the aqueous reaction mixture with various organic solvents including acetophenone and chloroform. Analyses and conductivity measurements in nitrobenzene indicated that the compound has the formula $[Ph_3MeAs]_2[Ni(C_2S_2O_2)_2]$.

In the micro-determination of nickel described in this paper, the proposed extracting solvent is a mixture of chloroform and acetophenone. The amount of chloroform may vary within the range 20% to 50% of the mixture without affecting the result. If chloroform is present in amounts less than 20%, the solvent layer separates from the aqueous layer too slowly; when present above 50%, low results may be obtained due to the relatively low solubility of the ion association compound in chloroform.

Amounts of triphenylmethylarsonium chloride or potassium dithio-oxalate solutions within the range of half to three times those specified afforded constant readings. With the arsonium chloride, amounts above this limit resulted in a loss in efficiency of extraction of the ion association compound. The potassium dithio-oxalate solution need not be freshly prepared. Such a solution is green and cloudy and could not possibly be used if an extractive technique were not employed.

Extraction can be performed from aqueous solutions of pH 3 to 8. Above pH 8 the bis-dithio-oxalato nickelate(II) ion does not form immediately; for pH values below 3, high readings are obtained due to the extracting solvent becoming cloudy.

The ion association compound shows very satisfactory stability in the extracting solvent. It was extracted from aqueous solutions having pH values over the range 3 to 8, and the maximum changes observed in Spekker reading after 2 h and 75 h were 0.5% and 2.5% respectively. The greatest stability occurred in the region of pH 4 to 5, the change in readings being zero after two hours and only 1% after 75 h. A solution of the bis-dithio-oxalato nickelate(II) ion in water at approximately the same pH showed a 2% change in 2 h and a 25% change after 50 h. The solutions were kept away from light, the bis-dithio-oxalato nickelate(II) ion being slightly photosensitive. However, this sensitivity to light was not sufficient to cause significant errors in the method, as a solution, extracted from an aqueous layer of pH 4 to 5, showed a reduction in reading of only 0.3% when exposed to light for two hours at 20°, and of 1% at 30°.

The transmission curve of $[Ph_3MeAs]_2[Ni(C_2S_2O_2)_2]$ in the mixed solvent shows an absorption maximum at 505 mμ and a minimum at 404 mμ. These correspond to the maximum and minimum absorptions of the complex ion bis-dithio-oxalato nickelate(II) in aqueous solution.

The solution obeys Beer's Law within the suggested range of concentrations. Cobalt, copper and iron interfere. A simple, rapid method for their removal is suggested.

PROCEDURE

A volume (preferably not more than 25 ml) of solution containing from 25 to 250 μg of nickel is pipetted into a 100-ml separating funnel. The solution is tested with congo red paper and, if necessary, acid is added until the indicator paper turns blue. The pH of the solution is then adjusted to the most suitable range for the extraction by the addition of 3 to 5 ml of 10% sodium acetate solution in excess of that required to turn the indicator paper red.

The extracting solvent (a mixture of approximately 55% acetophenone and 45% chloroform by volume) (5 ml) is added to the separating funnel, followed by potassium dithio-oxalate solution (0.25%, 2 ml). Upon the addition of the latter, the aqueous layer turns red due to the formation of the bis-dithio-oxalato nickelate(II) ion. Triphenylmethylarsonium chloride solution (0.5%, 2 ml) is then added. The resultant compound is extracted into the organic layer, which is filtered, under suction, through

a sintered glass filter. The aqueous layer is extracted twice more with 5-ml volumes of the organic solvent, the filter is washed, and the filtrate and washing are made up to 25 ml in a graduated flask. The solution is then compared with a blank solution in a "Spekker" photoabsorptiometer using 1-cm cells, heat absorption filters H503 and green spectrum filters 604. The nickel content of the solution is then obtained by reference to a calibration curve prepared by treating a series of solutions of nickel of known concentration in the same manner as above.

RESULTS

Results obtained over the range 25 to 250 μg of nickel are shown in Table I. It may be seen that the average reproducibility is of the order of 1% or better, while the maximum deviation to be expected is approximately 2%.

TABLE I

Solutions containing 25 to 250 μg of nickel. Six samples taken at each concentration

Nickel present (μg)	*Nickel found (μg)* *min.*	*max.*	*Largest % error*	*Average error (6 readings)* μg	%
25.0	24.8	25.3	1.2	0.1	0.4
50.0	49.0	51.0	2.0	0.5	1.0
100.0	98.8	102.3	2.3	1.0	1.0
150.0	149.5	150.5	0.3	0.3	0.2
200.0	198.0	202.8	1.4	1.0	0.5
250.0	248.0	250.8	0.8	0.8	0.3

Weighed amounts of two nickel complexes were decomposed by wet ashing, diluted with distilled water, and aliquots analysed for nickel by the proposed method. The results are shown in Table II.

TABLE II

Compound	*% Nickel calculated*	*% Nickel found*	*Mean % nickel found*
A	11.95	11.8	12.0
		12.0	
		12.1	
		12.1	
B	11.55	11.7	11.5
		11.4	
		11.5	
		11.3	

INTERFERENCES

The effect of the presence of various ions was studied by introducing them into a standard solution containing 200 μg of nickel. The tolerance limit of an ion was fixed as the maximum amount causing a deviation no greater than 2% in the estimated

nickel content. If this was the case when the amount of the ion present was one thousand times that of the nickel, *i.e.* 200,000 μg, then the ion was stated to be non-interfering.

Anions

The anions sulphate, nitrate, chloride, bromide, acetate, carbonate and oxalate were found to be non-interfering. The triphenylmethylarsonium cation forms with thiocyanate[1-3] and with iodide ion-association pairs which are soluble in the extracting solvent. Consequently, when large amounts of these anions are present, additional arsonium chloride solution must be added prior to each extraction.

Cations

JONES AND TASKER[15] observed colour reactions in aqueous solution when potassium dithio-oxalate was added to certain ions of the following elements: Sb, Bi, Cd, Co, Cu, Fe, Mn, Hg, Ag, Sn, Pd, Pt, Zn, Ce, Au, Tl, Ti and V. The interferences caused by these elements in the present method were studied (Table III).

TABLE III

Quantity of nickel used = 200 μg

Cation	*Tolerance amount (μg) (Method as above)*	*Positive (+) or negative (−) interference*	*Ratio of tolerance amount to nickel amount*	*Tolerance amount (μg) (Method modified)*	*Positive (+) or negative (−) interference*	*Ratio of tolerance amount to nickel amount*
Co(II)	15	+	≏0.1	10,000 (*a*)	+	50
Fe(III)	8	+	≏0.05	4,000 (*a*)	+	20
Cu(II)	15	+	≏0.1	6,000 (*a*)	+	30
Zn(II)	Non-interfering					
Ag(I)	2,000	—	10	20,000 (*b*)	+	100
Sb(III)	Non-interfering					
Sn(II)	Negligible (*c*)					
Ce(IV)	4,000	—	20	20,000 (*b*)	+	100
Cd(II)	1,000	—	5	10,000 (*b*)	—	50
Mn(II)	20,000	+	100			
Hg(II)	2,000	—	10	20,000 (*b*)	—	100
Au(III)	2,000	—	10	20,000 (*b*)	—	100
Pd(II)	600	—	3	(*d*)		
Pt(IV)	20,000	—	100	(*d*)		
Bi(III)	Negligible (*c*)					
Tl(I)	2,000	—	10	8,000 (*b*)	—	40
V(V)	20,000	—	100	Non-interfering (*b*)		
Ti(IV)	Non-interfering					

Notes on Table III

(*a*) If cobalt, copper and/or iron are present, the procedure should be modified. When the pH of the nickel solution is just high enough to turn congo red paper red, chloroform (5 ml) is added, followed by 5% $Ph_3MeAsCl$ solution (5 ml; or 10 ml when iron is present) and 20% KSCN solution (1 ml; or 2 ml in the presence of iron). The thiocyanato complexes are removed by a total of three extractions with 5-ml volumes of chloroform. The general procedure for nickel is then followed with one

small alteration, necessitated by the large concentration of thiocyanate present. This alteration is the addition of 6 ml (10 ml for iron) of 0.5% $Ph_3MeAsCl$ solution prior to the first nickel extraction (instead of the 2 ml used in the general procedure), and the addition of 4 ml (6 ml for iron) before the second extraction.

The above modified method was used to achieve the tolerance amounts quoted in Table III. If smaller quantities of cobalt, copper and/or iron are present, the amounts of reagents used for their removal may be reduced. On the other hand, the tolerance amounts may be increased by increasing the quantities of reagents.

(*b*) 10 ml of $Ph_3MeAsCl$ solution (0.5%) and 20 ml of $K_2C_2S_2O_2$ solution (0.25%) were used.

(*c*) Precipitation of tin(II) and bismuth occurred upon adjustment of the pH to that used in the recommended procedure.

(*d*) Increasing the amounts of reagents as in (*b*) causes the interference by Pd(II) and Pt(IV) to change from negative to positive with no increase in tolerance. It is preferable to use only a small excess of reagent (*i.e.* the quantity specified in the procedure) when either of these elements is present.

SUMMARY

The colorimetric micro-determination of nickel described involves the formation of $[Ph_3MeAs]_2[Ni(C_2S_2O_2)_2]$ and its extraction into an organic solvent. As the extracted compound is strongly coloured, its concentration is measured without further treatment. The procedure given is suitable within a range of 25 to 250 μg of nickel with an average error no greater than 1%. Iron, cobalt and copper interfere seriously, and a simple method is suggested for their removal.

RÉSUMÉ

Une méthode colorimétrique est proposée pour le microdosage du nickel, sous forme de $[Ph_3MeAs]_2[Ni(C_2S_2O_2)_2]$ (bis-dithiooxalatonickelate(II) de triphénylméthylarsonium). Ce composé, extrait dans un solvant organique (chloroforme et acétophénone) est fortement coloré.

ZUSAMMENFASSUNG

Beschreibung einer colorimetrischen Methode zur Bestimmung kleiner Mengen Nickel durch Überführung in den Komplex $[Ph_3MeAs]_2[Ni(C_2S_2O_2)_2]$, der bei der Extraktion mit einem organischen Lösungsmittel eine stark gefärbte Lösung gibt. Störende Elemente und deren Entfernung werden erwähnt.

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MICRODOSAGE DE TRACES DE COBALT DANS LES CIMENTS PAR SPECTROPHOTOMÉTRIE

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INTRODUCTION

S'il est important de connaître le taux de cobalt d'une fonte, utilisée dans la construction des réacteurs, en tant qu'écran dit thermique, il peut également être intéressant de déterminer la teneur en cobalt des ciments entrant dans la composition du béton, utilisé comme écran, dit biologique.

Le ciment est un produit chimique artificiel dont les éléments suivants sont définis de façon assez précise: SiO_2, 20–24%; Al_2O_3, 6–9%; Fe_2O_3, 2–4%; CaO, 62–66%; MgO, 1–3%; SO_3, 1–1.5%; insoluble, 1%; non déterminé et perte au feu, 2%.

Les éléments contenus à l'état de traces ne sont pas indiqués car leur présence ne modifie pas les propriétés physiques et chimiques d'un béton. Par contre, lorsque ce béton est soumis à un flux de neutrons thermiques important, la présence de certains éléments à forte section efficace et donnant naissance à des radioisotopes de longue période, prend une grande importance. Le cobalt, par exemple, dont la section est de 36 barns et la période de son radioélément 60 de 1924 jours, peut donner au béton une radioactivité indésirable. Il est donc important de connaître la teneur exacte de cet élément dans le ciment.

Les principaux travaux concernant le dosage du cobalt dans des milieux semblables, comme les roches et les sols, sont essentiellement axés sur la spectrographie. En effet, LOUNAMAA[1] détermine le cobalt dans les roches silicatées par spectrographie, après extraction à la dithizone ou par le diéthyldithiocarbamate. PICKETT ET HANKINS[2] précipitent le cobalt contenu dans les sols, par l'oxine et le détermine ensuite spectrographiquement. Certains auteurs[3] précipitent, par l'acide rubéanique, les métaux lourds contenus dans les sols, puis séparent le cobalt au moyen de l'α-nitroso-β-naphtol avant de le doser polarographiquement. Enfin, SMALES *et al.*[4] soumettent les roches, les sédiments marins ou les météorites à un flux de neutrons thermiques et, après séparation du cobalt par précipitation au moyen de l'α-nitroso-β-naphtol, le dosent par une méthode radiochimique.

PRINCIPE DE L'ANALYSE, SOLUTIONS ET APPAREILLAGE

Le principe de la méthode que nous préconisons a déjà été l'objet d'autres applications, notamment celles du dosage du cobalt dans l'acier 18/8[5], dans la fonte[6], dans l'inconel[7], dans le zirconium[8] et dans le sang[9]. La même méthode peut également s'ap-

pliquer au dosage du cobalt dans l'aluminium et dans le ciment. C'est cette dernière que nous décrirons dans ce travail.

Après mise en solution dans l'acide chlorhydrique concentré, en présence de quelques gouttes d'acide nitrique afin d'oxyder Fe^{+2} en Fe^{+3}, la séparation du cobalt se fait en milieu HCl 9 *M*, par passage de la solution sur une résine échangeur d'ions. Le dosage proprement dit se fait par spectrophotométrie au moyen du sel nitroso-R (nitroso-1-hydroxy-2-naphtalène disulfonate-3,6 de sodium), méthode s'avérant la plus sensible, la plus précise et l'une des plus rapides lorsqu'il s'agit de doser des traces de cobalt[6,10].

Tous les réactifs utilisés sont des produits Merck, pro anal., soit : acide chlorhydrique concentré (12 *M*) et solutions 9 *M*, 4 *M* ainsi que 0.01 *M*. Acide nitrique concentré. Solution de chlorure de sodium à 5%. Solution tampon, acétate de sodium 10%, amenée au pH 6 par l'acide acétique glacial. Solution de sel nitroso-R 0.05%. Résine échangeur d'ions Dowex 1-X8 de 100 à 200 mesh (produit Flucka). ^{60}Radiocobalt, titrant 0.007 μg de Co par ml et d'une activité de 0.05 μC par ml. L'appareillage est constitué par une échelle décadique "Tracerlab" type SC 33 A, "1000 scaler", équipée d'un cristal à puits de NaI (Tl) de 5/5 cm. Spectrophotomètre Beckman, modèle DU, avec photomultiplicateur permettant l'extension de la zone de lecture à 90–100% de transmission sur toute la longueur de l'échelle.

MARCHE À SUIVRE

Mise en solution

0.05 à 0.5 g de ciment (Tableau I) sont introduits dans un tube à centrifuger de 30 ml, en même temps que 4 ml d'une solution de ^{60}Co, en milieu HCl 9 *M*, d'activité bien déterminée (préparée en diluant 1 ml de la solution de ^{60}Co décrite ci-dessus dans 3 ml de HCl conc.), le ^{60}Co sert de traceur et permet de déterminer les pertes au cours des opérations de mise en solution et de séparation. On ajoute ensuite 10 ml de HCl conc. et quelques gouttes d'acide nitrique conc. On laisse réagir en introduisant le tube dans un bain-marie bouillant jusqu'à ce qu'il ne reste plus qu'un résidu blanc floconeux (SiO_2) et que le dégagement de vapeurs nitreuses cesse (le volume final est d'environ 3 ml). On ajoute alors 10 ml de HCl 9 *M*, secoue et laisse refroidir la solution.

On centrifuge 30 min à 3000 t/m, décante la solution limpide qu'on introduit dans un bécher de 50 ml. Le résidu est lavé au moyen de 5 ml de HCl 9 *M* et on centrifuge une nouvelle fois 30 min dans les mêmes conditions que précédemment. La solution décantée est jointe à la précédente, le cobalt est prêt à être séparé par fixation sur résine échangeur d'ions. Pour ce qui concerne le résidu, voir page 367.

Préparation de la colonne échangeur d'ions

Suivant la prise initiale de ciment, la hauteur de la colonne active sera différente ainsi que son diamètre. Pour une prise de 0.5 g par exemple, nous avons utilisé une colonne de 15 cm de haut et de 0.8 cm de diamètre (~ 3 g de résine), tandis que pour 0.05 g, la hauteur était de 10 cm et le diamètre de 0.6 cm (~ 1.5 g de résine). Afin d'éviter un colmatage de la colonne par des particules de résine très fines, on ajoute à environ 10 g de résine brute, 100 ml d'eau bidistillée et on brasse la suspension. On laisse reposer et décante la liqueur contenant les fractions les plus fines. On répète cette opération 5 fois, puis on termine en ajoutant 100 ml de HCl 0.01 *M*. On introduit

alors une partie de la résine dans la colonne. Dans le fond de celle-ci, on dispose un tampon de laine de verre, un même tampon sera placé sur la résine après remplissage. La colonne est lavée au moyen de 20 ml de HCl 0.01 *M* pour éliminer toutes traces d'éléments minéraux, puis on la sature par 10 ml de HCl 9 *M*.

Si les dimensions de la colonne sont judicieusement choisies, celle-ci n'est saturée en ions Fe^{+3} (coloration brune de la résine) que dans sa partie supérieure et l'éluat contenant le cobalt sera suffisamment pur pour éviter toutes interférences dues aux éléments gènants lors du dosage spectrophotométrique du cobalt au moyen du sel nitroso-R.

Séparation du cobalt

La solution 9 *M* obtenue (voir *Mise en solution*) est introduite dans la colonne. Le temps de passage est d'environ une goutte toutes les dix secondes. On lave ensuite la colonne avec 10 ml de HCl 9 *M* afin d'entraîner les éléments qui n'y sont pas retenus soit, entre autres, les alcalins, les alcalino-terreux, le nickel, le chrome et l'aluminium. On effectue l'élution du cobalt en introduisant dans la colonne 15 ml de HCl 4 *M*. Ces 15 ml sont récupérés par fractions de 4 ml, dans des éprouvettes graduées de 6 cm de haut et 1 cm de diamètre. Nous mesurons l'activité de ces diverses fractions afin de savoir comment le cobalt se répartit entre elles. La majeure partie du cobalt se trouve dans la 2ème et la 3ème fractions, qui sont introduites dans une capsule de pyrex de 10 ml en présence de 0.5 ml de chlorure de sodium à 5% comme support. Après évaporation sous une calotte infra-rouge et refroidissement, on reprend le résidu, qui doit être blanc, par 2 ml d'eau bidistillée que l'on introduit dans un tube à centrifuger de 10 cm de haut et de 1.2 cm de diamètre, tube ayant servi à mesurer l'activité du ^{60}Co ajouté au ciment, avant sa mise en solution. On lave la capsule 2 fois avec 1 ml de solution tampon acétate de sodium 10%, amenée au pH de 6 au moyen d'acide acétique. Nous avons donc maintenant un volume de 4 ml (volume correspondant à celui que nous avions lors de la détermination de l'activité du ^{60}Co, ajouté au début). On mesure alors l'activité de ces 4 ml de solution et on peut déterminer exactement les pertes en cobalt lors des diverses opérations qu'on vient d'effectuer (Tableau II).

Dosage spectrophotométrique

Dans le tube à centrifuger, ayant servi à déterminer les pertes et contenant le cobalt à doser, on introduit 0.5 ml d'une solution de sel nitroso-R à 0.05%, fraîchement préparée, et on chauffe une minute au bain-marie bouillant. On introduit rapidement 0.5 ml d'acide nitrique concentré pour détruire une partie de l'excès de réactif et on chauffe dans les mêmes conditions que précédemment encore 30 sec. On refroidit le tube dans un courant d'eau et on amène le volume exactement à 5 ml avec de l'eau bidistillée. On centrifuge 20 min à 3000 t/m pour rendre la solution optiquement vide. La lecture de la densité optique ou de la transmission se fait sur environ 3 ml de solution dans des cuves de 1 cm d'épaisseur, la longueur d'onde étant de 520 mμ (Tableau III).

COBALT COMBINÉ À LA SILICE

La partie insoluble, formée par la silice (voir *Mise en solution*), peut contenir du cobalt combiné n'ayant pas passé en solution. Pour déterminer cette teneur en cobalt, nous avons lavé le résidu avec de l'eau bidistillée jusqu'à ce qu'il ne présente plus aucune

radioactivité provenant du ^{60}Co ajouté (ce qui nous permet d'affirmer que le cobalt qui s'y trouverait encore n'est plus ionique, mais bien combiné à la silice). La mise en solution du résidu s'effectue de la façon suivante: introduire dans un creuset de platine en même temps que du ^{60}Co comme traceur, ainsi que 0.5 ml de NaCl 5% comme support, 10 ml d'acide fluorhydrique concentré, par petites portions, en évaporant à sec après chaque adjonction d'acide. Reprendre par HCl 9 *M* (tout doit passer en solution). Procéder alors comme décrit sous *Dosage spectrophotométrique*.

Nous avons pu constater que le cobalt trouvé peut être négligé (3% au plus) par rapport au cobalt total, et ceci pour tous les échantillons analysés.

RÉSULTATS OBTENUS

Nous avons déterminé la teneur en cobalt de ciments de provenances diverses, que nous désignerons par C_r, C_v, C_m et C_e. Le Tableau I nous indique les prises effectuées pour chaque échantillon de ciment.

TABLEAU I

POIDS DES DIVERSES PRISES

Ciment	*Analyse No.*	*Prise g*	*Ciment*	*Analyse No.*	*Prise g*
	1	0.50119		7	0.51518
C_r	2	0.10037	C_m	8	0.10083
	3	0.05012		9	0.08736
				10	0.05155
	4	0.48894		11	1.01364
C_v	5	0.10127	C_e	12	0.52558
	6	0.05030		13	0.47463
				14	0.09917

TABLEAU II

PERTES AU COURS DES DIVERSES OPÉRATIONS

Analyse No.	^{60}Co *ajouté c.p.m.*	^{60}Co *retrouvé c.p.m.*	*Perte %*	*Analyse No.*	^{60}Co *ajouté c.p.m.*	^{60}Co *retrouvé c.p.m.*	*Perte %*
1	43435	39656	8.9	11	43521	41258	5.2
2	42656	40566	4.9	12	42856	39856	7.0
3	43777	42289	3.4	13	43348	39620	8.6
				14	43612	42086	3.5
4	43259	41399	4.3				
5	43441	42225	2.8	15	43871	42818	2.4
6	43632	42541	2.5				
				16	43438	42091	3.1
7	43748	41867	4.3	17	43283	42071	2.8
8	43462	42071	3.2				
9	43958	40353	8.2				
10	43687	41459	5.1				

Le calcul des pertes a été fait en comparant l'activité du ^{60}Co ajouté au début et celle retrouvée juste avant le dosage spectrophotométrique. Le Tableau II rend compte des pertes pour toutes les analyses effectuées sur les ciments (1–14); pour une solution

à blanc (sans ciment) ne contenant que les réactifs utilisés et ayant été soumise à toutes les opérations (15); et deux essais (également sans ciment) mais contenant une quantité de cobalt bien déterminée (16, 17).

Le Tableau III rend compte des résultats obtenus. Toutes les analyses (1–17), ont été comparées à une solution ne contenant que les réactifs utilisés pour le dosage spectrophotométrique, soit la solution tampon, le sel nitroso-R et l'acide nitrique.

TABLEAU III

RÉSULTATS DES DIVERSES ANALYSES

1	2	3	4	5	6	7	8
Ciment	*Analyse No.*	*Densité optique D*	*Co trouvé µg*	*Co corrigé (perte) µg*	*Teneur % (×10⁻⁴)*	*Moyenne % (×10⁻⁴)*	*Erreur relative %*
	1	0.20981	4.280	4.688	9.354		
C_r	2	0.04579	0.934	0.982	9.787	9.55	±2.5
	3	0.02269	0.460	0.477	9.510		
	4	0.19334	3.044	4.121	8.429		
C_v	5	0.04029	0.822	0.846	8.351	8.44	±1.2
	6	0.02053	0.419	0.430	8.540		
	7	0.10064	2.053	2.145	4.164		
C_m	8[d]	0.02130	0.435	0.449	4.452	4.41	±5.9
	9	0.01719	0.351	0.382	4.371		
	10	0.01120	0.228	0.241	4.670		
	11	0.44853	9.150	9.652	9.522		
C_e	12[d]	0.23627	4.820	5.183	9.861	9.70	±1.8
	13	0.20381	4.158	4.549	9.584		
	14	0.04605	0.939	0.974	9.815		
blanc[a]	15	0	—	—	—	—	—
témoin[b]	16	0.11618	2.370	2.446	—	—	—
témoin[c]	17	0.04598	0.938	0.965	—	—	—

[a] Blanc, ne contenant que les réactifs et ayant passé par toutes les opérations.
[b] Témoin ne contenant que les réactifs et 2.46 µg de cobalt, ayant passé par toutes les opérations.
[c] Témoin comme [b] mais contenant 0.954 µg de cobalt.
[d] Prises auxquelles nous avions respectivement ajouté 0.954 µg (analyse 8) et 2.46 µg (analyse 12) de cobalt comme étalon interne. Dans les valeurs des densités optiques correspondantes, nous avons déjà tenu compte de ce cobalt ajouté.

Les valeurs de la colonne 4 du Tableau III sont obtenues en multipliant les densités optiques inscrites dans la colonne 3 par le facteur 20.4. Ce facteur s'obtient en multipliant le volume final, soit 5 ml par 4.08. Cette dernière valeur représente le rapport de la concentration en cobalt, par ml de solution, sur la densité optique (rapport constant, déterminé au moyen d'une courbe d'étalonnage). Dans la colonne 5, nous donnons la quantité de cobalt trouvée pour les diverses prises, en ayant tenu compte des pertes indiquées dans le Tableau II. Dans la colonne 6 sont incrits les % de cobalt contenu dans chaque prise et dans la colonne 7, la teneur moyenne en % de l'échantillon. La dernière colonne donne l'erreur relative.

CONCLUSION

Le dosage du cobalt dans les ciments que nous avons étudiés, a révélé que sa teneur

pouvait varier entre 0.0004 et 0.0010%, suivant la provenance de l'échantillon. L'erreur est inférieure à 6%. Ce dosage peut se faire encore facilement sur une prise de 0.05 g et un volume de 5 ml au moment de la mesure spectrophotométrique.

La durée des opérations pour une telle analyse est d'environ 6 h (en tenant compte de la préparation de la colonne échangeur d'ions). Le temps nécessaire pour effectuer une série de 10 analyses reste à peu près le même que celui utilisé pour une seule. Aucune précaution spéciale n'a été prise pour éviter les pertes, puisqu'elles n'entachent pas les résultats du fait qu'elles sont exactement déterminées (^{60}Co). Ces pertes sont d'ailleurs inférieures à 10%. D'autre part, nous n'avons pas pris en considération, lors de l'élution, les fractions ne renfermant que de très faibles quantités de cobalt.

REMERCIEMENT

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RÉSUMÉ

Une méthode de dosage de traces de cobalt dans les ciments est décrite. La séparation se fait sur résine échangeur d'ions Dowex 1-X8 et le dosage proprement dit par spectrophotométrie au moyen du sel nitroso-R comme réactif complexant. Les pertes au cours des diverses opérations sont exactement déterminées par marquage du cobalt au moyen de ^{60}radiocobalt. La quantité de cobalt contenue dans les échantillons étudiées varie entre 0.0004 et 0.0010%, avec une erreur relative inférieure à $\pm$ 6%.

SUMMARY

Description of a method for the determination of traces of cobalt in cements, by separation by means of an exchange resin followed by spectrophotometric determination with nitroso-R salt.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Spuren von Kobalt in Zementen. Sie beruht auf der Trennung mit Hilfe eines Austauscherharzes und anschliessender spektrophotometrischer Bestimmung des Reaktionsproduktes mit Nitroso-R Salz.

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THE DETERMINATION OF PLUTONIUM BY MASS SPECTROMETRY USING A [242]-PLUTONIUM TRACER

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INTRODUCTION

In recent years the isotopic dilution method has been used increasingly for the determination of uranium and thorium, but apart from a few single determinations described by HART *et al.*[1] the technique does not appear to have been applied to the determination of plutonium. This is somewhat surprising for such a method should be both specific and precise. There is a general need for an accurate method for sub-microgram quantities of plutonium, and one obvious application is the determination of plutonium in fuel element dissolver solutions. This paper describes an isotopic dilution method using highly enriched ^{242}Pu as the tracer.

CHOICE AND CALIBRATION OF TRACER

The plutonium under analysis consisted mainly of ^{239}Pu with 3–4% of ^{240}Pu, ~0.2% ^{241}Pu and very small quantities of ^{238}Pu and ^{242}Pu (0.005–0.01%).

The isotopic dilution method involves the addition of a known mass of tracer to a known mass of sample, a step to ensure that the sample and tracer plutonium are in the same chemical form, and then an isotopic analysis for the mixture. Thus the most suitable tracer will be the one satisfying the following conditions:

(*1*) its isotopic composition should be as different as possible from that of the sample under analysis, (*2*) its use should involve a minimum of interference from other elements.

In the absence of ^{244}Pu, the isotopes which may be considered for use as tracers are ^{238}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu. Of these ^{241}Pu and ^{238}Pu may be rejected for the following reasons. The use of ^{241}Pu represents a serious health hazard, the nuclide has a short half-life (13 years) and its mass spectrum may be complicated by traces of ^{241}Am. ^{238}Pu may be prepared by irradiation of ^{241}Am and produced in a state of high isotopic purity[1,2], but its use for the present work is not advisable for interference could be caused by ^{238}U. To guarantee an error of less than 0.1% would require a chemical separation factor of the order of 10^6, and moreover, as the abundance of ^{235}U is low (0.5–1%) it would be difficult to use this isotope as a monitor for uranium contamination. These criticisms of course only apply to a method based on mass spectral analysis, and not to one involving α-pulse analysis[1].

Both ^{240}Pu and ^{242}Pu could be used for the required determination. The method described by HART *et al.*[1] involved the use of a ^{240}Pu tracer (^{239}Pu, 61%; ^{240}Pu, 33%; ^{241}Pu, 4.6%; ^{242}Pu, 1.1%), and more highly enriched material (97%) has been pre-

pared by electromagnetic separation in Hermes[3]. However ^{242}Pu may also be prepared in a state of high isotopic purity and in view of the isotopic composition of the samples, this nuclide was selected for use as the tracer. The material used had been prepared by prolonged irradiation of ^{239}Pu in a high flux reactor. The irradiation of 350 mg plutonium for several years produced only 6–7 mg of ^{242}Pu[4], but as an adequate mass analysis can be made with 0.1 μg of plutonium, even 1 mg of tracer would be sufficient for 10,000 single determinations. μg quantities of ^{242}Pu of 98–99% purity have also been prepared by two day irradiations of americium[2].

About 200 μg of ^{242}Pu were kindly supplied by Dr. J. MILSTED, Chemistry Division, A.E.R.E., Harwell. It had the following isotopic composition: ^{238}Pu, 0.3%; ^{239}Pu, 0.4%; ^{240}Pu, 0.5%; ^{241}Pu, 0.2%; ^{242}Pu, 98.4%; ^{244}Pu, 0.2%. This material was diluted to a concentration of ~0.1 μg/g in 3 *N* nitric acid, and calibrated accurately against a ^{239}Pu standard. The concentration determined in this way does not involve a knowledge of the chemical purity of the tracer, and in addition mass discrimination errors are eliminated.

EXPERIMENTAL DISCUSSION

The solutions under analysis had been prepared with the following approximate composition: U, 300 mg/ml; Pu, 100 μg/ml; fission product γ-activity 25 mC/ml. Thus in outline a determination consists of (*1*) diluting a solution to a suitable concentration, (*2*) mixing an aliquot with a suitable aliquot of tracer, and then ensuring that complete exchange has taken place, (*3*) separating plutonium from uranium, and (*4*) mounting the plutonium on a mass spectrometer source unit for an isotopic analysis.

The original solution was diluted to a concentration of ~0.1 μg/g in 3 *N* nitric acid in two stages, the overall dilution factor being ~1000. For any individual determination a 2-g aliquot of dilute solution (containing ~0.2 μg ^{239}Pu) was weighed into a polythene bottle followed by a 2-g aliquot of tracer. After thorough shaking about one half of this solution was taken for analysis; the other half was retained so that a repeat determination could be made if required. A portion of solution containing 0.2 μg plutonium contains only 50 μC of fission product γ-activity, so apart from the first dilution, which was made behind a 2" lead wall, no difficulty was introduced by the radiation hazard.

An essential requirement of the isotopic dilution method is that the sample and tracer element should be mixed thoroughly, and in the case of plutonium this implies the need for a step to ensure that the two forms are in the same valence state. This point has also been stressed by HART *et al.* For each determination they prepared a mixture of sample and tracer in 7–11 *N* nitric acid and then allowed it to stand for 4–5 days to reach isotopic equilibrium; they did not make a detailed study of this process but stated that it requires some considerable time. They considered two of their five values to be suspect because isotopic equilibrium was not certain. In the present work a two stage process was used to achieve isotopic equilibration. The mixture of sample and tracer in 3 *N* nitric acid was evaporated to dryness. The residue was dissolved and reduced with hydroxylamine hydrochloride in hydrochloric acid. The resultant solution was evaporated to dryness, its residue redissolved in concentrated nitric acid, and then this solution evaporated to dryness. This final stage both destroys hydroxylamine and oxidises the plutonium to the tetravalent state. The final residue was dissolved in 8 *N* nitric acid and an ion exchange separation made.

An aliquot of solution containing 0.1 μg plutonium also contains 300 μg uranium and 25 μC fission product γ-activity. It is essential to separate plutonium from the bulk of the uranium, for otherwise the large uranium ion beam at mass number 238 might reduce the quality of the plutonium mass spectrum. It is also desirable to remove the fission product activity in order to avoid cumulative contamination of the mass spectrometer. The method selected involved the use of small ion exchange columns of De-acidite FF. Solutions were applied in 8 *N* nitric acid, and uranium and fission products washed through with further portions of 8 *N* nitric acid. It was found necessary to use a minimum of seven washes to remove uranium completely, probably to ensure thorough washing of the glass walls above the resin. Plutonium was then eluted with 0.1% hydroxylamine hydrochloride, 1 *N* hydrochloric acid solution. In assessing the separation plutonium was determined by α-counting, uranium by fluorimetry and fission product activity by γ-counting. Plutonium recoveries were usually better than 90%, and contamination by uranium and fission products was $<0.01\%$ and $<1\%$ of the quantities added respectively. Thus the final product separated from an aliquot of one of the samples might consist of 0.1 μg ^{239}Pu, 0.01–0.03 μg uranium, and 0.1–0.2 μC of fission product γ-activity. The ion exchange columns were of a design that could not run dry, but consequently they were somewhat slow. Normally six columns were operated together.

The plutonium fraction collected from the columns was evaporated to small volume, and then transferred dropwise to a siliconed indented microscope slide, each drop being evaporated to dryness under an infra-red lamp. The deposit on the slide was then treated with a few drops of nitric acid to destroy hydroxylamine. This procedure usually produced a clearly visible spot in the centre of the slide. The plutonium was then removed with a small quantity of water and transferred to the sample filament of a mass spectrometer source unit.

Isotopic analyses were made with an Associated Electrical Industries Ltd. type M.S.5 mass spectrometer. The filament assemblies were modified slightly (by bending the kovar stems) to make the sample filament point towards the centre filament, thereby improving the geometry (and possibly the sensitivity) of the arrangement. Large uranium ion beams were usually observed at the beginning of each isotopic analysis, but by slowly increasing the temperature of the sample filament uranium could be evaporated from the filament without any significant loss of plutonium; in the isotopic analyses finally recorded ^{238}U was usually only a few per cent of the ^{239}Pu ion beam. This process required about 30 min and was conveniently combined with the procedure for minimising hydrocarbon background[5]. Forty to fifty ratios were usually recorded for each isotopic analysis.

About two days were required for the treatment of six samples, including weighing and mixing aliquots of tracer and dilute sample, separation of plutonium, and preparation of mass spectrometer sources. This could probably be reduced somewhat by using smaller and simpler ion exchange columns. Mass analyses were made at the rate of two per day.

ANALYTICAL PROCEDURE

Reagents

8 *N* nitric acid; 0.1% hydroxylamine hydrochloride, 1 *N* hydrochloric acid; 20% (w/v) hydroxylamine hydrochloride; De-acidite FF (200 mesh).

Ion exchange columns

Approximately 40 mg (~0.1 ml) of dry De-acidite FF is retained in 3-mm (i.d.) glass tubing by a constriction and a glass wool plug 10–12 cm from the upper end. The tubing below the constriction is bent up and then over, and drawn off to give an outlet at a suitable height to prevent the column from running dry. A shorter length of 6-mm (i.d.) tubing fused to the upper end provides a suitable reservoir. The complete unit is washed with three successive 2-ml volumes of 8 *N* nitric acid, and then used once only.

Method

Solution, standard and tracer are prepared in 3 *N* nitric acid at a concentration of ~0.1 μg plutonium/g.

Weigh about 2 g of tracer solution and 2 g of sample accurately into clean dry polythene bottles (20 ml) and mix thoroughly by shaking vigorously for 1 min. Transfer about 2 g of the mixture to a 30-ml beaker and evaporate carefully, without boiling, just to dryness. Dissolve the residue in about 2 ml of 1 *N* hydrochloric acid, 0.1% hydroxylamine hydrochloride solution and add 3 drops of 20% hydroxylamine hydrochloride solution. Evaporate again to dryness, and then add 2 ml of concentrated nitric acid and warm to destroy excess hydroxylamine. Evaporate just to dryness, dissolve the residue in 2 ml of 8 *N* nitric acid and transfer to an ion exchange column. Allow the solution to pass through the column and then apply eight successive 2-ml washes of 8 *N* nitric acid. Elute plutonium from the column with three successive 1-ml volumes of 0.1% hydroxylamine hydrochloride, 1 *N* hydrochloric acid, collecting the eluate in a "tall-form" 5-ml beaker. Evaporate under an infra-red lamp to a volume of about 0.3 ml and then transfer dropwise to a "siliconed" indented microscope slide placed under an infra-red lamp. Allow each drop to evaporate to dryness before applying the next one. In this way the residue can be concentrated within a small area. Add a small quantity of concentrated nitric acid, and evaporate to dryness to destroy hydroxylamine. Transfer the residue with a small quantity of water to the sample filament of a mass spectrometer source unit. A simple *alpha* monitor may be used to check the efficiency of this transfer.

Results

Results were calculated using the following equation:

$$w = y(R_M - R_T) \cdot \frac{239}{242} \cdot \frac{100}{P} \cdot \frac{\text{mass tracer solution}}{\text{mass dilute sample}} \cdot D$$

where: w is concentration of total plutonium in original solution,
D is dilution factor,
P is mass percentage of ^{239}Pu in sample,
y is concentration of ^{242}Pu in tracer solution,
R_M is $^{239}Pu/^{242}Pu$ ratio for the mixture of sample and tracer,
R_T is $^{239}Pu/^{242}Pu$ ratio for the tracer.

Results for the calibration of the ^{242}Pu tracer are presented in Table I. Tables II and III list results for the concentration and isotopic composition respectively for

four samples. Columns 5 and 6 in Table II record the coefficients of variation (of a single value, and of the mean value) for the determinations of R_M; concentration values marked by an asterisk are discussed in a later section.

TABLE I

CALIBRATION OF ^{242}Pu TRACER

Concentration ^{242}Pu μg/g	*Mean value*	*Coefficient of variation:*	
		single value	*mean value*
0.0842			
0.0843			
0.0843			
0.0844	0.0844 μg/g	0.15%	0.06%
0.0845			
0.0845			
0.0846			

TABLE II

RESULTS FOR CONCENTRATION OF Pu

Solution	*Concentration Pu μg/g*	*Coefficient of variation*		*Precision of mass analysis* %	
		single value %	*mean value* %		
	103.0			1.24	0.19
	103.2			0.48	0.08
1	103.2			0.72	0.11
	103.3*			1.29	0.18
	103.4			0.81	0.13
	103.2	0.14	0.06		
	116.8			1.18	0.18
	117.1			0.69	0.10
2	117.3			0.52	0.08
	117.4			0.63	0.09
	117.4			0.49	0.08
	117.2	0.23	0.10		
	118.8			0.82	0.14
	118.8			1.07	0.20
3	118.9			0.46	0.07
	119.0			0.41	0.06
	119.2			0.74	0.14
	118.9	0.15	0.07		
	120.9			0.70	0.11
	120.9*			0.58	0.08
4	121.0*			0.57	0.07
	121.0			0.76	0.14
	121.4			0.60	0.08
	121.0	0.18	0.08		

* Values labelled by an asterisk are referred to at foot of p. 378.

DISCUSSION OF RESULTS

The sources of random error in a determination consist of both the mass spectrometric errors tabulated above, and those associated with the dilution of samples, and the

TABLE III

ISOTOPIC COMPOSITION OF SAMPLES

Solution	*Isotopic analyses (atomic percentages)*		*Mass percentage ^{239}Pu*	*Coefficient of variation (for mean value) %*
1	^{239}Pu	96.24	96.23	0.008
	^{240}Pu	3.57		
	^{241}Pu	0.19		
	^{242}Pu	$\geqslant$ 0.015		
2	^{239}Pu	96.10	96.08	0.010
	^{240}Pu	3.70		
	^{241}Pu	0.20		
	^{242}Pu	$\geqslant$ 0.006		
3	^{239}Pu	95.96	95.94	0.006
	^{240}Pu	3.83		
	^{241}Pu	0.21		
	^{242}Pu	$\geqslant$ 0.05[a]		
4	^{239}Pu	96.01	95.99	0.012
	^{240}Pu	3.78		
	^{241}Pu	0.21		
	^{242}Pu	$\geqslant$ 0.01		

[a] A later analysis gave $^{242}Pu \geqslant 0.005\%$.

preparation and dilution of the standard solution. These may be summarised as follows (all errors are expressed in the coefficient of variation form):

(*a*) *Calibration of tracer.* A standard solution was prepared by dissolving ~1 g of plutonium metal (mainly ^{239}Pu) in hydrochloric acid and diluting accurately to a concentration of ~0.1 μg/g. Weighed aliquots of this solution were mixed with weighed aliquots of tracer, and plutonium was separated using the procedure described on page 374. The various sources of error are as follows: mass of plutonium, 0.03%; 100-ml flask, 0.02%; 10-ml pipette, 0.10%; 1-l flask, 0.02%; 10-ml pipette, 0.10%; 1-l flask, 0.02%, 10-ml pipette, 0.10%; ~100 g of solution, negligible; 3 × standard error for mass spectrometric calibration, 0.17%; 3 × standard error for mass percentage of ^{239}Pu in standard, 0.02%. Thus the overall error for the calibration is 0.25%.

(*b*) *Determinations.* 1-ml aliquots of the solutions of irradiated uranium were diluted to 100 ml, and 10-ml aliquots of these solutions diluted to ~100 g. For each sample five weighed aliquots of these dilute solutions were then mixed with weighed aliquots of tracer, and the determinations made as described above; one aliquot was taken directly and used for a determination of the isotopic composition of the sample. The various sources of error are as follows: 1-ml pipette(3 σ), 0.14%; 100-ml flask, 0.02%; 10-ml pipette, 0.10%; ~100 g of solution, negligible; 3× standard error for mass spectrometric determination, 0.24%; 3× standard error for mass percentage of ^{239}Pu in samples, 0.03% (the last two entries represent mean values for the four solutions). Total value, 0.30%.

The overall value (3 σ) for a determination including calibration errors is 0.39%. This error may be considered in three parts: the mass spectrometric error for the calibration, the mass spectrometric error in the determination, and dilution errors etc., both for the solution under analysis and for the standard. These three values are

0.17%, 0.24% and 0.25% respectively. Thus the overall dilution error quoted here is in fact comparable with the two mass spectrometric errors, and it is also possible that it may be an underestimate. Apart from the 1-ml pipette which was calibrated experimentally, the dilution error has been assessed by using either grade A limits or Emil "green line" limits for flasks and pipettes; these have been assumed to represent $3\times$ standard deviation of a single value. In fact these errors may be underestimates since past experience with 10-ml pipettes indicates a value of ~0.15% for $3\times$ coefficient of variation of a single value, compared with the value used above of 0.10%.

In addition to the consideration of random errors given above, it is also necessary to establish that no significant error has been caused by the presence of the nuclides ^{238}Pu, ^{242}Pu, ^{241}Am and ^{242}Cm. It would for example be very difficult to detect small quantities of ^{238}Pu in these samples by mass spectrometry. Thus for ^{238}Pu contents in the range 0.1%–0.01% of total plutonium it would require a separation factor from uranium of the order of 10^7–10^8 to ensure that a mass number 238 ion beam was derived essentially from plutonium, and even if this were achieved there would remain the question of the small quantities of uranium present as an impurity in the mass spectrometer filament material. However ^{238}Pu may be determined quite readily by α-pulse analysis, and these samples contained only ~0.005%.

In the calculation of results it has been assumed that the ^{242}Pu content of the samples is zero. A search for the presence of this isotope was made in each of the simple isotopic analyses, but a mass analysis can be complicated by the presence of background peaks in this region. In one case the background peak at mass number 242 was equivalent to an abundance of 0.05% ^{242}Pu, but by repeating this analysis and by examining the isotopic analyses for the other samples it was concluded that the ^{242}Pu content is certainly not greater than 0.01%, and probably not greater than 0.005%.

The nuclides ^{241}Am and ^{242}Cm could not introduce significant errors for their concentration in the samples under analysis was very low, and they would also be separated from plutonium by the ion exchange stage.

Thus it may be concluded that if the determinations described in this paper are accepted as typical, the method described offers a precision (three standard errors) of 0.4% for determinations of submicrogram quantities of plutonium based on five replicate analyses, provided that considerable care is taken to prevent the introduction of errors by uncertainties in the dilution factors.

POSSIBLE APPLICATION TO FUEL ELEMENT DISSOLVER SOLUTIONS

In view of the high precision of the technique it is worth examining its potentiality as a routine method. For example, it could be applied to the feed solution of a chemical processing plant designed to extract plutonium from irradiated fuel elements of natural or slightly enriched uranium as, for example, the Windscale primary separation plant. In this respect it may be noted that the composition of the samples used for this work approaches that of a typical feed solution, for the uranium concentration is comparable with the value quoted for the Windscale plant, and the plutonium content is about one third of the Windscale value[6]. The problem of analyses for dissolver solutions was considered recently by SHULTS *et al.*[7]; they concluded that controlled potential coulometric titration was the most promising method, and quoted

precisions (1 σ) of 0.1% for 1 mg of plutonium, 0.3% for 250 μg, and 1.5% for 50 μg. However, the isotopic dilution method appears capable of giving a precision approaching the best reported for coulometric titration, and for the analysis of dissolver solutions it could also provide the following advantages: (*1*) it requires such a small quantity of plutonium (0.1 μg) that the radiation level presents no problem (with the possible exception of the initial dilution); (*2*) it is subject to a minimum of interference from other elements; (*3*) it does not require a quantitative separation of the plutonium. In this case the interest would lie in the precision of a single determination. For the four sets of results listed in Table II the coefficients of variation for a single value are 0.14%, 0.23%, 0.15%, and 0.18% respectively, giving a mean value of 0.17%. If a procedure is envisaged in which two aliquots are taken from a solution under analysis, one to be used for a determination by the addition of tracer, and the other to give the isotopic composition of the plutonium, then the corresponding value of one standard deviation, including errors from the calibration, etc., would be 0.2%.

The use of the method on a routine basis would require some control over analyses in order to maintain a suitable standard of precision, and it would be valuable if some criteria for an acceptable analysis could be indicated. Errors may arise from evaporation or from uncertainties in the masses of sample or tracer taken, but these may be minimised by careful work. The largest single contribution to random error is likely to be the uncertainty in the mass analysis, and for this it is possible to give a more quantitative description. For each individual plutonium determination the isotope ratio R_M was based on the mean value for a mass spectrometric analysis involving about 40 ratios. The coefficient of variation of these values about their mean, and also that of the mean value are given in the last column of Table II; these have been calculated simply from the relation: standard deviation = 1.25 $\times$ mean deviation. The mean value of the standard error for a mass analysis is 0.12% which is at least a substantial portion of the mean standard deviation of 0.17% for the plutonium determinations. Moreover there is some correlation between the standard error of a mass analysis and the corresponding result. Thus if for any set of five results a weight is assigned to each value proportional to the reciprocal of [relative standard error of mass analysis]^2, then the coefficient of variation for the mean value of the set of five results may be calculated as

$$\sqrt{(\Sigma W_i d_i^2)/(n-1)\,\Sigma W_i}$$

Values found in this way for the four samples are 0.05%, 0.08%, 0.05%, 0.08% (mean value 0.065%) compared with the directly calculated values of 0.06%, 0.10%, 0.07% and 0.08% (mean value 0.078%).

Thus the mass spectrometric analyses used for this work had coefficients of variation in the range 0.4–1.3% (mean value 0.75%) and were based on approximately forty ratios. In addition the intensity of ion beams rarely decreased by more than 50% over the course of the analysis, and usually the changes were much less than this. Sections of scans containing, or recorded immediately after H.T. instabilities were rejected. Ion currents were usually of the order of $2\text{–}3 \cdot 10^{-14}$ A.

With the exception of the three results indicated by an asterisk in Table II, the mass analyses used were those produced directly by the mass spectrometer. For the three exceptions the initial mass analysis was rejected and the determination repeated

for the following reasons. In the first case ion source instabilities developed during the analysis, and the mass spectrometric record could be divided into two sections. The first had a standard deviation of 0.72% (24 ratios) and gave a result of 103.06 μg/ml; for the second part the equivalent figures were 2.1% (14 ratios) and 101.8 μg/ml. By taking a weighted average a value of 102.98 μg/ml was obtained, but it was considered preferable to reject this result and to repeat the analysis. The other two results were obtained when the Honeywell-Brown recorder had been returned from "servicing". The instrument showed no response to small changes in the input signal and as a result the correct peak height was not necessarily plotted. The standard deviations and values of the rejected results were: 1.6% (36 ratios), 122.0 μg/ml; 1.0% (39 ratios), 121.7% μg/ml. The fault was eventually traced to incorrect mechanical assembly of the recorder.

In view of the high enrichment of the ^{242}Pu tracer, a possible extension of the method might be a combination of the isotopic analysis for sample plutonium with the isotopic dilution determination into one mass spectral analysis. This should be feasible for samples of the type described in this paper where the ^{242}Pu content is negligible, and the possibility was examined in one single determination. When sufficient data had been recorded to provide the usual forty estimates of the ^{239}Pu/^{242}Pu ratio, the mass analysis was continued, by recording the ^{240}Pu and ^{241}Pu isotopes on a sensitive range of the amplifier, to give ten estimates of the ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu ratios. In this one case the isotopic composition calculated by correction for the presence of tracer is ^{239}Pu, 96.11%; ^{240}Pu, 3.70%; ^{241}Pu, 0.185%, compared with the values ^{239}Pu, 96.10%; ^{240}Pu, 3.70%; ^{241}Pu, 0.195%, obtained by a complete isotopic analysis for a portion of "unspiked" sample. In the application of such a method to plant analyses it would be necessary to consider also the build-up of ^{242}Pu with increasing irradiation time. Values have been published for the isotopic composition of plutonium produced at various irradiation levels of natural uranium in the NRX reactor[1]. By comparison with these data the samples described in this report would correspond to an irradiation approaching ~1000 MWD/tonne. At higher irradiation levels the abundance of the ^{242}Pu isotope would increase, but even at irradiations approaching 3000 MWD/tonne it is only of the order of 0.1–0.2%, and this could probably be calculated sufficiently accurately to avoid the need for an independent determination.

CONCLUSIONS

The isotopic dilution technique has been applied to the determination of plutonium in solutions of irradiated uranium and appears to offer the following advantages:

(1) *High precision.* The precision (3σ) for a result based on one isotopic dilution determination combined with one isotopic analysis for the sample is $\pm$ 0.6%; for five replicate analyses the value is $\pm$ 0.4%.

(2) *Determinations require only 0.1 μg plutonium.* The fission product γ-activity associated with this quantity of material is small, perhaps only of the order of 25 μC, and as a result the chemical treatment is simplified, for no undue precautions against the radiation hazard are involved.

Apart from a general requirement for precise methods of determination for submicrogram quantities of plutonium, one specific application of the technique could be its use for control analyses of feed solutions in chemical plants, analogous to the

method used at the Idaho chemical processing plant for uranium[8]. If this were to be established there are two obvious extensions of this work: (*1*) An examination of the precision for determinations of the isotopic composition of the sample plutonium in the presence of the tracer. If satisfactory this might permit a complete determination to be made by one mass spectral analysis. (2) For analyses of the type described in this paper dilution errors could represent a significant part of the overall uncertainty. These might well be larger if the method were applied routinely to a plant, but a procedure could be envisaged in which they would be eliminated. Thus a scheme involving the addition of a mixture of tracers of uranium and plutonium might be applied to the determination of U/Pu ratios, and these used with the total input of uranium (possibly determined by weight) to give the plutonium input to the plant.

These two possibilities have been examined and will be discussed in a subsequent paper.

SUMMARY

An isotopic dilution method is described for the determination of plutonium in samples of irradiated uranium using a ^{242}Pu tracer. An aliquot of tracer is added to the sample and the mixture treated to ensure isotopic exchange; plutonium is then separated by an ion exchange procedure and an isotopic analysis made using an M.S.5. mass spectrometer. The precision (3σ) for an aliquot containing 0.1 μg plutonium is 0.6%. A possible application of the method would be its use for control analyses of the feed solution in a chemical plant processing natural uranium fuel elements as, for example, the Windscale primary separation plant.

RÉSUMÉ

Une méthode par dilution isotopique est décrite pour le dosage du plutonium dans des échantillons d'uranium irradié; le ^{242}Pu est utilisé comme traceur. Le plutonium est séparé par échangeur d'ions; l'analyse isotopique a été effectuée au moyen d'un spectromètre de masse M.S.5.

ZUSAMMENFASSUNG

Beschreibung einer Isotopenverdünnungsmethode zur Bestimmung von Plutonium in bestrahltem Uranium mit ^{242}Pu als Tracer. Die Abtrennung des Plutoniums erfolgt mit einem Austauscherharz.

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POLAROGRAPHIC MAXIMA AND SOLUTION MOVEMENTS

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Observations of solution movements associated with polarographic maxima made by ANTWEILER[1] and by KRYUKOVA AND KABANOV[2] indicate vigorous, well-defined and reproducible motions that often extend for distances equal to several times the diameter of the drop. KRYUKOVA observed both upward and downward motion. Downward motion was limited to maxima occurring on the positive side of the electrocapillary zero. Upward motion occurred with maxima at potentials on the negative side of the electrocapillary zero. In one case, namely that of a negative maximum, KRYUKOVA observed a reversal of direction of motion produced by changing the ratio of concentration of reducible ion to supporting electrolyte.

ANTWEILER has suggested that the stirring originates in an electrical disturbance occurring on the surface of the mercury drop. He has observed a rapid irregular vibration of the surface of the mercury drop and describes the solution movement resulting as "electrostatic stirring".

It has been shown[3] that polarographic currents become excessive whenever the solution about the drop is agitated. Thus we have a probable explanation of the immediate cause of the increased current but the ultimate cause of the solution movements is still obscure. The present paper presents additional information describing the phenomenon of motion and contributes to the existing theories of maxima.

It has been observed in this investigation that both upward and downward motion were displayed by solutions of potassium ferricyanide, at the potential of the maximum. In 0.001 *M* ferricyanide–0.1 *M* potassium chloride solutions, the motion was entirely upward. In a 0.005-*M* solution the motion was entirely downward. By choosing concentrations of ferricyanide between 0.001 *M* and 0.005 *M* a concentration was found at which the solution motion around the growing drop was upward during the first part of the drop's growth and became downward during the latter part of the growth. At the point of reversal there is a momentary motionless appearance in the solution. The concentration of the ferricyanide in the solutions showing the reversal of motion was from 0.0025 *M* to 0.003 *M*. The drop time of the capillary used was 3.5 sec.

Subsequent experiments showed that for capillaries of different drop times, either reversal failed to occur at the same concentration or else the proportion of upward to downward motion was very different. It was also found that for a given concentration of an ion it was possible to produce a change in direction of the motion by changing the drop time of the capillary. For a solution of 0.001 *M* ferricyanide in

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0.1 *M* potassium chloride a downward motion was observed through the maximum when the drop time was 5.5 sec. When the drop time was changed to 3.2 sec by changing the pressure on the capillary, the observed motion was entirely upward. An intermediate drop time of 4.5 sec gave an upward motion during the first part of the drop's growth and reversed to a downward motion during the latter half.

Examples of reversal were also observed for the maxima obtained with solutions of copper, lead and oxygen in 0.1 *M* potassium chloride. Table I gives a summary of the types of motion observed. When the supporting electrolyte was omitted the reversal of the motion could not be detected for solutions of copper, ferricyanide, lead, nickel or iodate ions, in concentrations ranging from 0.001 to 0.01 *M*.

An unusual type of motion was found for copper solutions containing 0.1 *M* potassium chloride. In addition to some vibrational motion, rapidly rotating eddies of solution were seen to move perpendicularly away from the surface of the drop.

TABLE I

SOLUTION MOTIONS ASSOCIATED WITH MAXIMA

Solution	*Drop time (sec)*	*Types of motion*[a]
0.0001 *M* $K_3Fe(CN)_6$ + 0.1 *M* KCl	1–3.5	1
0.0025 *M* $K_3Fe(CN)_6$ + 0.1 *M* KCl	3–3.5	4
0.005 *M* $K_3Fe(CN)_6$ + 0.1 *M* KCl	3–3.5	2
0.001 *M* $K_3Fe(CN)_6$ + 0.1 *M* KCl	4.5	4
0.001 *M* $K_3Fe(CN)_6$ + 0.1 *M* KCl	5.5–9	2
0.001–0.01 *M* $K_3Fe(CN)_6$	3–9	2,6
0.0001 *M* $K_3Fe(CN)_6$	3–5.5	2,4
0.0005–0.001 *M* $CuSO_4$ + 0.1 *M* KCl	2.7–3.2	1
0.001–0.01 *M* $CuSO_4$ + 0.1 *M* KCl	4.5–5.5	2,3
0.0001–0.01 *M* $CuSO_4$	3–5.5	2,3
0.001–0.005 *M* $Pb(NO_3)_2$ + 0.1 *M* KNO_3	3–3.5	1
0.001–0.005 *M* $Pb(NO_3)_2$ + 0.1 *M* KNO_3	5.5	2
0.001–0.005 *M* $Pb(NO_3)_2$	3–3.5	1
0.001–0.005 *M* $Pb(NO_3)_2$	5.5	2
0.001–0.01 *M* $NiCl_2$ + 0.1 *M* KCl	3–9	1,5
0.001–0.01 *M* $NiCl_2$	4–5	1
0.001–0.01 *M* $CoCl_2$ + 0.1 *M* KCl	3–4	1
0.001–0.01 *M* KIO_3 + 0.1 *M* KCl	3–3.5	1
0.001–0.01 *M* KIO_3	4–5	1
Distilled water saturated with O_2	3	1
Distilled water saturated with O_2	4–9	2
Distilled water only	3–9	No motion
0.1 *M* KCl saturated with O_2	4	2
0.1 *M* KCl partially saturated with O_2	4	1
0.1 *M* KCl saturated with O_2	5.5	2
0.1 *M* KCl saturated with O_2	3.2	1
0.1 *M* KCl only	3–9	No motion

[a] 1. Entirely upward
2. Entirely downward
3. Vibrational and whirling
4. First upward, then downward
5. First upward, then motionless
6. Motionless, then downward

EXPERIMENTAL

In the experimental work, solution movements were made evident by the presence of carbon particles in the solution. Their motion was observed through a low power microscope focussed on the drop. A Sargent Model polarographic instrument with photographic current recorder was used for applying both fixed and gradually increasing potentials. Electrode potentials were measured against a calomel half-cell using a supplementary potentiometric circuit. "Analytical" grade reagents were used for all solutions. A motion picture record was made of all solution movements and was used for the repeated study of each motion.

DISCUSSION

Previous theories proposed for the explanation of maxima do not account for the reversals in motion on the positive side of the electrocapillary zero when the concentration of the reducible ion and the drop time are changed. Repeated observations have shown that the upward motions found with maxima occurring on the positive side of the electrocapillary zero are the same in appearance as those on the negative side. That is, if one were not aware of differences in the solutions being examined and in the applied potentials, one could not distinguish between the two examples of motion. This leads to the proposition that the surface condition in the two cases is the same during the upward motion.

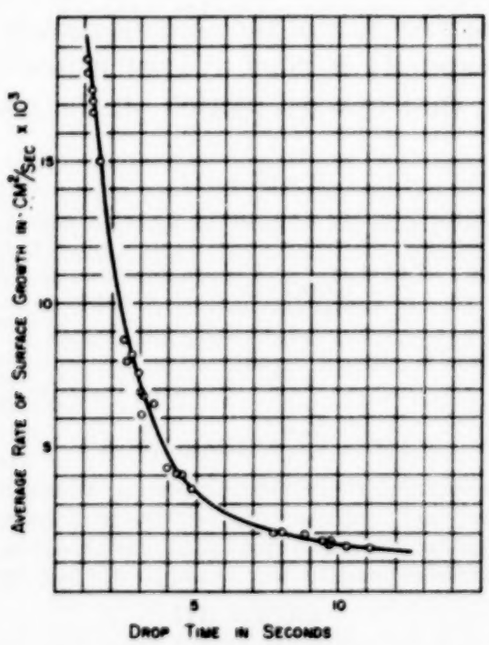

Fig. 1. Average rate of surface growth as a function of drop time.

The facts that the motion can be reversed from downward to upward by decreasing the drop time and that reversal from upward to downward can be observed during the life of a single drop suggest a factor which varies with the drop time and during the life of a single drop. Such a variable is the rate of surface growth of the mercury drop. It not only changes with drop time, being greater at shorter drop times, but also changes during the growth of a single drop as shown in Fig. 1. The surface grows

noticeably faster when the drop is small at the beginning of the drop growth. Thus it seems that *upward* motion is associated with a rapidly growing surface.

The concentration at which reversal was observed was not the same for capillaries of different drop times. The ratio between the concentration of reducible ion and the rate of surface growth was calculated for ferricyanide and copper ions for the examples of reversal noted for each. From the data there is an indication of the existence of a critical ratio between concentration of the reducible ion and growth rate. For ferricyanide, a ratio of 0.26 has been found where *both upward and downward* motion are observed and for the cupric ion the ratio is about 0.18. For ratios less than these the motion is largely downward and *vice versa*.

In attempting to explain the change in direction of motion which has been observed, certain observations appear valid starting points. There is no difference in the general appearance of the upward motion of a positive maximum and the upward motion associated with a negative maximum. The assumption will then be made that the surface characteristics in both instances of upward motion are the same.

The surface of mercury when in contact with water or an aqueous salt solution carries a positive charge. When it is connected in a circuit and a potential applied, stepwise, the surface charge is made less positive and at an applied potential of —0.56 V, the surface is uncharged. When mercury is in contact with glass it is negatively charged with respect to the glass. This means that at the interface there is an orientation of negatively charged particles on the mercury surface to offset a positive orientation of the glass. This negative character of the surface is the same as that for drops on the negative side of the electrocapillary zero. When the mercury flows from the tip of the capillary it must at least momentarily carry this negative charge. It has been shown that upward motion on the positive side of the electro-

TABLE II

SURFACE GROWTH RATE DATA AND DIRECTION OF MOTION FOR $K_3Fe(CN)_6$ IN 0.1 *M* KCl

Molar conc.	*t (sec)*	*Growth rate* $(cm^2/sec)\cdot 10^3$	*Ratio* $= \frac{conc.}{Growth\ rate}$	*Direction of motion*
$1\cdot10^{-3}$	5.5	3.15	0.314	downward
$1\cdot10^{-3}$	4.5	3.8	0.263	both
$1\cdot10^{-3}$	3.2	6.8	0.147	upward
$2.5\cdot10^{-3}$	2.6	8.5	0.294	downward
$2\cdot10^{-3}$	2.75	7.8	0.256	both
$1\cdot10^{-3}$	2.8	7.7	0.130	upward

TABLE III

SURFACE GROWTH RATE DATA AND DIRECTION OF MOTION FOR $CuSO_4$ IN 0.1 *M* KCl

Molar conc.	*t (sec)*	*Growth rate* $(cm^2/sec)\cdot 10^3$	*Ratio* $= \frac{conc.}{Growth\ rate}$	*Direction of motion*
$2.5\cdot10^{-3}$	2.7	8.25	0.304	downward
$1\cdot10^{-3}$	4.4	3.85	0.260	downward
$1.6\cdot10^{-3}$	2.7	8.25	0.195	both
$1.3\cdot10^{-3}$	2.85	7.5	0.173	both
$1\cdot10^{-3}$	2.95	7.3	0.137	upward
$0.5\cdot10^{-3}$	2.7	8.25	0.061	upward

capillary zero is associated with a rapidly growing surface. This suggests that a time factor is involved in establishing conditions for a normal orientation of charge such as exists on the positive branch of the capillary curve. For example, if mercury is leaving the tip more rapidly than the surface charges can be oriented it retains a negative character temporarily and the motion will be that usually associated with maxima on the negative side of the capillary zero, namely upward.

The two following observations serve to further substantiate the above explanation. (1) The intensity of the upward motion occurring on the positive side of the electrocapillary zero diminishes as the drop grows even when there is no sign of reversal of motion during the life of the drop. In other words, the drop appears to be losing its charge. (2) When a reversal of motion occurs during the life of a single drop there is a momentary stopping of motion which makes it appear as though a maximum suppressor were present; that is, there is momentarily no oriented surface charge.

SUMMARY

Solution movements during the existence of polarographic maxima have been made evident by suspending carbon black in the solution. Only upward motion is observed with maxima occurring on the negative side of the electrocapillary zero. Both upward and downward motion occur with positive maxima. Examples are found in which both upward and downward motion occur during the life of a single drop. Upward motion is associated with the early life of the drop during which the rate of surface growth is greater and also with drops having a shorter life time and hence a greater growth rate. For the two ions $Fe(CN)_6^{-3}$, and Cu^{+2}, a critical ratio of concentration to growth rate exists below which upward motion prevails and above which downward motion prevails. The motions and their directions are considered due in part to the negative character of the mercury surface as it leaves the glass capillary, the time interval for the mercury surface to lose its negative orientation, and the attraction of the ions of the solution by the non-uniformly charged surface.

RÉSUMÉ

On a pu mettre en évidence, au moyen de noir de carbone en suspension, les mouvements produits dans la solution pendant l'existence des maxima polarographiques. Lorsque le maximum se trouve du côté négatif du zéro électrocapillaire, on observe seulement un mouvement vers le haut, tandis que les maxima positifs donnent lieu à des mouvements de bas en haut et de haut en bas. Dans certains cas les deux mouvements peuvent avoir lieu pendant la vie d'une seule goutte. Le mouvement vers le haut est en relation avec la première période de vie de la goutte, pendant laquelle la vitesse d'accroissement de la surface est plus grande, et aussi avec la présence de gouttes à vie plus courte, ayant par conséquent une plus grande vitesse d'accroissement. Des essais ont été effectués avec les deux ions $Fe(CN)_6^{-3}$ et Cu^{+2}.

ZUSAMMENFASSUNG

Die bei polarographischen Maxima auftretenden Strömungsbewegungen der Lösung konnten durch Zugabe von Kohleteilchen sichtbar gemacht werden. Die beobachteten Strömungsrichtungen werden beschrieben und deren Entstehung durch den wechselnden Charakter der Quecksilberoberfläche und seinen Einfluss auf die Ionen in der Lösung erklärt.

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Short Communications

Ethyl dithiocarbamate as a substitute for hydrogen sulphide

Hydrogen sulphide is an invaluable reagent in qualitative inorganic analysis but when it is used in the gaseous form, it is troublesome and unpleasant to handle, and the conditions are not readily controlled. Therefore, in recent years, several reagents have been proposed as substitutes for hydrogen sulphide. Thioacetamide has been recommended[1] in aqueous solutions and is of some merit in qualitative chemical analysis, but it has several disadvantages[2]. Modifications have been proposed but these are rather complicated[2].

In a search for reagents to replace hydrogen sulphide, it has been found that ethyl dithiocarbamate is very suitable. It gives characteristic precipitates with definite colours which can be used for the identification of cations, and with a proper choice of conditions and hydrogen ion concentration, group separations are possible. The final colours of the precipitates are similar in most cases to those obtained with hydrogen sulphide but there are intermediate shades of colour and particle size before the final change which seem helpful for the identification of the ions. The reagent is a liquid and its addition can be easily controlled. It is readily prepared and can be stored for a fairly long time without much precaution.

The reagent was prepared by the gradual addition of carbon disulphide to ethylamine (33% w/v), the mixture being cooled after each addition to prevent volatilisation of the carbon disulphide; the reaction evolves much heat. After the reaction was complete, the unreacted carbon disulphide was removed on a water bath. The formation of the product was tested for by its catalytic effect on the iodine-azide decomposition, by precipitation of black silver sulphide from a solution of silver nitrate, and by the formation with cupric salts, of black precipitates insoluble in acetic acid and ammonia.

Various cations were examined with the following results:

Mercury(I). The white finely divided precipitate is almost white in the cold but becomes yellowish on warming. It is soluble in excess reagent but a black precipitate appears on heating. It is insoluble in acetic and hydrochloric acids and in ammonia but a change occurs with caustic soda.

Lead(II). The pale yellow gelatinous precipitate turns black on warming without any intermediate change of shade. The precipitate is insoluble in excess reagent and in dilute nitric acid but is appreciably soluble in the moderately concentrated acid.

Mercury(II). The initial white precipitate turns grey on further addition of the reagent and becomes black on warming. It is not attacked by acids but is rather soluble in caustic alkalies.

Bismuth(III). The flocculent yellow precipitate becomes brownish yellow on warming. It is insoluble in excess reagent or in acids.

Cadmium(II). The white gelatinous precipitate is insoluble in excess reagent but turns bright yellow on warming. It is insoluble in moderately concentrated acids.

Arsenic(III). The flocculent white precipitate becomes yellow or yellowish orange on warming; it remains yellow on cooling. The precipitate dissolves in excess reagent on heating to give a yellow solution from which a yellow precipitate separates on cooling. The precipitate is insoluble in concentrated acids, except nitric acid, but soluble in concentrated alkalies and ammonium carbonate.

Antimony(III). The initial yellowish gelatinous precipitate becomes yellow-orange on warming. The precipitate is insoluble but turns immediately orange in excess of the reagent; no precipitate appears on cooling the hot supernate. The precipitate is insoluble in acetic acid and ammonia but appreciably soluble in concentrated hydrochloric acid and in moderately concentrated alkalies.

Tin(II). A yellow precipitate with a tinge of orange is immediately formed. The precipitate yields a colourless solution with excess of the reagent in the cold; a precipitate is not formed on heating but is formed on acidification. The precipitate is soluble in moderately concentrated acids and alkalies but not in dilute acids or ammonia.

Cobalt(II). The greyish green precipitate, which is formed at pH 5.5–6 or in alkaline buffered solution, dissolves on warming to form a greenish yellow solution from which the same precipitate reappears on cooling. The precipitate is insoluble in excess of the reagent in the cold but on warming forms the same greenish yellow solution.

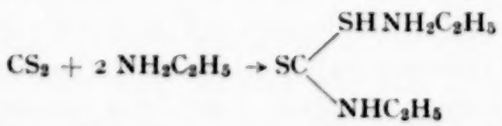
Nickel(II). The yellow-brown flocculent precipitate formed from acidic medium is insoluble in excess of the reagent or on warming.

Manganese(II). The greyish yellow precipitate first formed darkens in shade on further addition of the reagent; the ambient solution assumes a slightly reddish tinge which turns yellow on warming. The precipitate dissolves in excess of the hot reagent; on cooling sparkling yellow crystals separate. The crystals are insoluble in dilute mineral acids and in acetic acid.

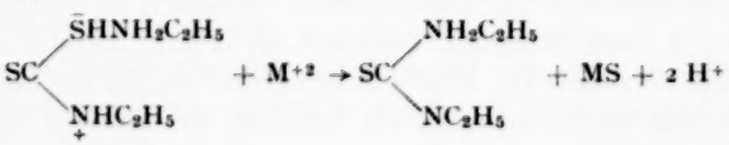
Zinc(II). The flocculent white precipitate is insoluble in excess of the reagent and does not change colour on heating. The precipitate is soluble in mineral acids but insoluble in acetic acid.

All the precipitates formed were either sulphides or hydrated sulphides which changed to the sulphides on warming or standing. Hence the reagent acts as a source of hydrogen sulphide.

The reagent is the end product of the interaction of carbon disulphide and ethylamine and contains the acidic SH-group and the basic NH-group attached to the same carbon atom:



There is probably interaction of these groups with the liberation of hydrogen sulphide particularly in ionogenic solvents. Several equilibria may exist, but the fundamental reaction is probably:



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Preparation of high specific activity tin-125 radiotracer

The separation of tin in trace amounts from geological materials and its determination colorimetrically using dithiol[1] may be monitored using radioactive 9.4 day ^{125}Sn tracer. By adding a measured amount of high specific radioactivity tracer to each sample and measuring the radioactivity of the final solution for colorimetry, each analysis is monitored for the chemical recovery of the element being determined, and a chemical yield correction may be applied. This technique has been employed in the analysis of iron meteorites[2] where it was not possible to achieve complete separation of tin from the dissolved specimen. Chemical yields, based on the radioactivity of the tracer recovered, were usually between 80% and 90%.

The nuclide 9.4 day ^{125}Sn, an emitter of 2.37 meV β^--radiation and low intensity γ-rays[3], can be prepared in high yield as a fission product of thorium or uranium by bombardment with cyclotron charged particles. It is separated from a solution of the bombarded target by distillation with hydrogen chloride and bromide from a sulfuric–phosphoric acid mixture as described by FARNSWORTH AND PEKOLA[1]. A target of thorium metal was bombarded in the Philips synchrocyclotron, Amsterdam, with deuterons, allowed to cool for 24 h, and dissolved in hydrochloric and nitric acids. Tin was then separated by distillation[1] and stored in a 6 *N* hydrochloric acid stock solution. The purity of the tracer was tested by decay and by measurement of the aluminium absorption curve. The half-life, measured over a period of 28 days using an end-window G-M counter, was 9.9 days, consistent with a mixture of the two fission products 9.4 day tin-125 and 130 day tin-123. An aluminium absorption curve, analyzed by Feather analysis, gave a range of 1180 mg/cm^2 and an energy of 2.4 meV for the energetic ^{125}Sn β^--ray, in agreement with the literature[3].

FARNSWORTH AND PEKOLA[1] showed that the distillation procedure was effective in separating tin from bismuth, iron, copper, nickel, cobalt, mercury, silver, lead, cadmium, arsenic, antimony and manganese, all of which react with the colorimetric reagent dithiol. Among elements not considered by them, selenium was found to accompany tin in the distillation procedure and to interfere in the colorimetric determination by roughly 1% for equal weights of selenium and tin, but the elements tellurium, germanium, thallium, gold and rhenium do not interfere. In the distillation of the tin radiotracer, however, none of these elements contribute contaminating radioactivity.

ACKNOWLEDGEMENTS

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A system for the determination of oxides of nitrogen

A report from this laboratory was recently published on a system for the determination of nitrates, and oxides of nitrogen[1]. Since then it has been found possible to simplify and improve the design of this system so that less manipulative procedures are involved and a more direct determination is obtained. The revised system is depicted in Fig. 1. The material to be analyzed may be introduced as a gas at NO_2, or if the material is a liquid or a solid, it may be thermally decomposed in the reaction tube A. For the metal nitrates presently being studied the materials are decomposed at 1000°, by employing a quartz envelope at A.

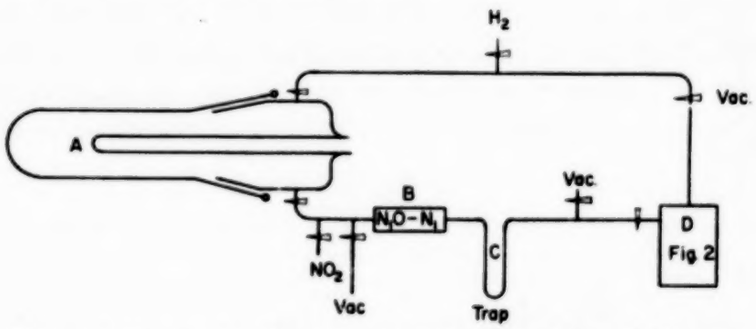

Fig. 1. A system for the determination of oxides of nitrogen.

The ensuing gases are allowed to pass out of the reactor tube A and through the tube B which contains metallic nickel maintained[1] at 800°. Oxygen resulting from oxides of nitrogen (NO_2, N_2O, NO, N_2O_3) and molecular oxygen are retained as nickel oxide. Nitrogen resulting from these oxides is allowed to pass through trap C, maintained at liquid nitrogen temperature, to the pump D where the volume of nitrogen is established. If it is desired to further segregate the oxide of nitrogen, a trap is introduced preceding tube B and is used to condense NO_2, N_2O_3. In this manner, NO_2 and N_2O_3 are retained in the trap maintained at liquid nitrogen temperature, while NO and N_2O will pass through the system for determination.

The nitrogen is collected by the pump in the calibrated bulbs, designated $D_{1,2}$ in Fig. 2. On conclusion of the complete collection of the nitrogen this gas pressure is measured by the pressure difference between the two arms of the manometer A_1 (maintained under vacuum) and $A_{2,3}$. From the known volume of $D_{1,2}$ and the pressure, it is possible to obtain directly the mole quantity of nitrogen either by use of the ideal gas law or by desired corrected equations of state. The run for nitrogen is concluded by discarding the nitrogen to the vacuum via stopcock B_1. The manometer is now ready to undertake the next step in the determination.

Hydrogen is now volumetrically manometered into the analytical system and allowed to circulate through the system, now using the Toepler pump as a circulator. Stopcock B_1 is rotated so that as the pump cycles, the gas will pass through the reaction system A and over the nickel oxide in tube B. During this process, water resulting from the reduction is retained in trap C. When reduction is complete (this may be followed via the manometer system) stopcock B_1 is closed and the residual hydrogen is collected as in the case of nitrogen and the residual volume of hydrogen is obtained. The difference between the initial and final volume of hydrogen gives a direct measure of the quantity of oxygen retained by the nickel oxide in tube B. From this information the composition of the nitrogen oxide gases can be established.

For a gas sample of 20 ml STP it is possible to obtain a reproducibility of 1% of a bulb volume ($D_1 + D_2$) 50 ml, and 1–1/4% on a bulb volume of 35 ml (D_1).

The pump employed in this work has a number of important features[2]; in particular, the facility of automatic pumping and circulation of gases as well as the manometering of the collected gases. Gas which enters the pump at the point indicated "gas in",

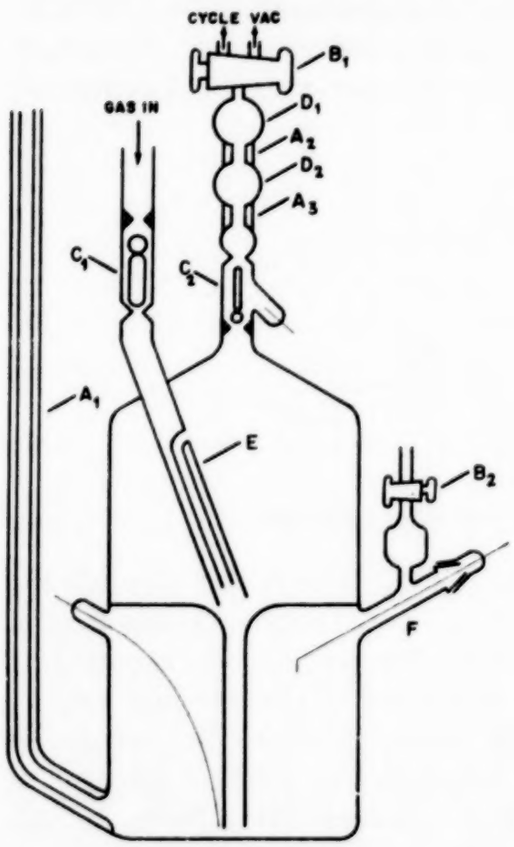

Fig. 2. Modified Toepler pump-manometer. A_1, 2-mm capillary manometer arm; $A_{2,3}$, 2-mm capillary tubing; B_1, three way vacuum bulb stopcock; B_2, vacuum bulb stopcock to relay system; $C_{1,2}$, float valves; $D_{1,2}$, manometer bulbs; E, high pressure entrance to Toepler pump; F, reversing probe.

pass through the entrance tube E and fill the upper chamber of the pump. The gas is then compressed as the mercury in the lower chamber is allowed to rise into the upper chamber. Contact to the mercury pool is made through lead wires F, which are adjustable, a terminal wire to the base of the pump, and the wire found at C_2. These wires lead to solenoid activated valve and pump. The gas may be gathered in bulbs $D_{1,2}$ and manometered or they may be allowed to circulate by rotating stopcock B_1 to the "open to the system" position.

This system is presently being used in a study of the interaction of NO_2 and certain metallic oxides.

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Gravimetric determination of thorium using some carboxylic acids

Numerous carboxylic acids have been reported from time to time as precipitants for thorium[1]. We have investigated the use of some other synthetic carboxylic acids for the determination and separation of thorium. At pH 2.6–3.4, thorium can be determined by means of dihydro-, 3,4-methylenedioxy-, and 3,4-methylenedioxy-dihydrocinnamic acids, while at pH 3.8–4.2, *o*-methoxycinnamic, thiosalicylic and *o*-bromobenzoic acids can be employed. As the tetra salts of thorium of these acids could not be isolated, the determinations were completed by ignition to thoria.

Of these acids, *o*-bromobenzoic acid was further found to be useful for the separation of thorium from rare earths. The separation of thorium could be effected at pH 3.9–4.8 from samples containing rare earths (R_2O_3) in amounts four times that of thoria; larger proportion of rare earths necessitates a second precipitation. Table I shows the results of a few representative experiments.

TABLE I

SEPARATION OF THORIUM FROM RARE EARTHS USING *o*-BROMOBENZOIC ACID

ThO_2 taken	*R_2O_3 added*	*ThO_2 found*	*Colour of thoria*
0.0448	0.0448	0.0448	White
0.0448	0.0896	0.0447	White
0.0448	0.1344	0.0449	White
0.0448	0.1782	0.0450	White
0.0448	0.2240	0.0451	White
		0.0447	White
0.0448	0.2689	0.0475	
		0.0447	White

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Buchbesprechungen

Gravimetrische Methoden der chemischen Analyse, LÁSZLÓ ERDEY, Akadémiai Kiadó, Budapest, 1960. Band I: *Theorie und Verfahrenstechnik der gravimetrischen Analyse*, 346 Seiten, Preis 85.— Ft. Band II: *Bestimmung der Metalle*, 739 Seiten, Preis 180.— Ft. Band III: *Bestimmung der Nichtmetalle*, 383 Seiten, Preis 90.— Ft. (Original: Ungarisch).

Das Buch bietet eine vollkommen erschöpfende Übersicht der gravimetrischen Analyse und enthält alle wichtigen physikalisch- und kolloidchemischen Kenntnisse, die zum Verständnis einiger gravimetrischer Handgriffe, besonders aber der theorie der Fällung von Niederschlägen bedeutend sind. Die einzelnen gravimetrischen Verfahren werden nicht bloss zusammengefasst, sondern auch kritisch bewertet. Dies bedeutet, dass der Leser in der analytischen Literatur erstmals eine äusserst grosse Anzahl von kritisch ausgewählten und durch Versuche kontrollierten Verfahren findet. Es wird somit dem in der Praxis tätigen Analytiker die Möglichkeit geboten, stets das am besten geeignete Verfahren zur Lösung eines konkreten Problem heranzuziehen.

Einer der Vorteile der Bücher von ERDEY ist, dass diese für einen weiten Interessentenkreis geschrieben wurden und daher sowohl Anfängern als auch Fachleuten Kenntnisse bieten, die bei der experimentellen Arbeit und zum Verständnis der theoretischen Probleme der Gravimetrie unbedingt benötigt werden.

Band I. Der Verfasser bespricht hier den Gang der gravimetrischen Analyse, von der Probenahme über den Aufschluss und die sonstigen vorbereitenden Operationen bis zum Auflösen des Stoffes, weiter die Ausfällung der Niederschläge mit allen einwirkenden Faktoren, sowie das Problem der Filtration und des Trocknens werden eingehend behandelt. Zur Untersuchung der Niederschläge von theoretischen Gesichtspunkten ist die Thermogravimetrie bzw. die verschiedenen Zweige dieses Verfahrens heute bereits unentbehrlich. Das Buch beschäftigt sich auch mit diesem Gebiet, dessen wissenschaftlicher und praktischer Bedeutung entsprechend.

Den zweiten Teil des I. Bandes widmet der Verfasser den Trennungsverfahren. Neben seiner vorzüglichen theoretischen Begründung leistet dieser Teil auch dem praktischen Analytiker wertvolle Hilfe, da er ein breites Spektrum der verschiedensten Trennungsmöglichkeiten kritisch behandelt. Eine kurze Zusammenfassung über die Elektrogravimetrie findet man gleichfalls in diesem Teil des Werkes. Am Ende des I. Bandes gibt ERDEY eine kurzgefasste, jedoch gut übersichtliche Beschreibung der gravimetrischen Wasseranalyse, sowie der Eigenschaften der verscheidenartig gebundenen Wässer.

Band II. Die Möglichkeit der gravimetrischen Bestimmung der Metallionen wird von ERDEY in der Reihenfolge des qualitativen Analysenganges behandelt. Bei den einzelnen Metallionen wird eine einführende, und die Übersicht der Bestimmungsverfahren erleichternde tabellarische Zusammenfassung gegeben. Die in diesen Tabellen enthaltenen literarischen Zitate ermöglichen ein rasches Nachschlagen in den Quellenarbeiten. Vom Standpunkt der Niederschlagsbehandlung sind die im Buch enthaltenen und theoretisch gut begründeten Thermoanalysen von Bedeutung. Bei

den einzelnen Ionen folgen auf die kritische Übersicht der verschiedenen Verfahren die Trennungsmethoden. Dieser Teil der Arbeit darf für den Routineanalytiker als besonders wertvoll angesehen werden, weil ERDEY die, in der Praxis am meisten vorkommenden Probleme, die der Trennung von den wichtigsten Begleitionen behandelt. In diesem Zusammenhang werden selbstverständlich eine Reihe analytischer Kunstgriffe angeführt.

Der Verfasser behandelt nachdrücklich die Richtlinien der L. W. WINKLER'schen gravimetrischen Verfahrenstechnik, ohne jedoch einseitige Anschauungen zu vertreten.

Band III. In diesem Bande werden die Verfahren zur gravimetrischen Bestimmung der Anionen einer eingehenden Untersuchung unterworfen. Es wird die Analyse von Cl, Br, J, F, CN, SCN, S, N, P, C, Si und B enthaltenden Verbindungen in Anwesenheit der am häufigsten vorkommenden und störenden Komponenten behandelt und die Lösung der in der Praxis am meisten auftretenden Probleme gegeben. Der Band enthält eine gute Zusammenfassung der Bestimmung des in organischen Verbindungen befindlichen Schwefels und Chlors.

Der Anhang des Buches fasst alle jene Kenntnisse zusammen die von der Reinigung der Geräte über die zur Fällung angewandten Reagenzien bis zur Berechnung der Analysenergebnisse führt, welche also ein Analytiker unbedingt benötigt. Am Ende des Buches sind die wichtigsten stöchiometrischen Faktoren enthalten.

Ein unentbehrliches Handbuch für jeden, der sich mit gravimetrischer Analyse beschäftigt. Es leistet sowohl dem angehenden Analytiker, als auch dem Fortgeschrittenen wertvolle Hilfe bei seiner Arbeit.

E. PUNGOR (Budapest)

Gmelins Handbuch der anorganischen Chemie, 8. Auflage, *Barium (Ergänzungsband) System Nr. 30*, 1960, iv, xlv, 569 Seiten, 76 Figuren, Verlag Chemie G.m.b.H., Weinheim/Bergstrasse, Kartoniert DM 354.—, Ganzleinen DM 359.—.

Der Ergänzungsband zu dem 1932 erschienenen Band *Barium* umfasst die Forschungsergebnisse von 1933 bis 1949. Der Anzahl der in dieser Periode durchgeführten Forschungsarbeiten entsprechend ist der Band wesentlich umfangreicher geworden als das Hauptwerk. Ausser dem Element Barium werden in diesem Band die Verbindungen des Bariums mit den Nichtmetallen und den Metallen As, Sb, Bi, den Erdalkalimetallen Be, Mg, Ca und Sr sowie den Alkalimetallen behandelt. Mehr als ein Drittel des Bandes befasst sich mit dem Vorkommen des Bariums in europäischen und ausser-europäischen Lagerstätten, in der Lithosphäre, Hydrosphäre und Biosphäre (Tier- und Pflanzenwelt). Im Kapitel über die Technologie des Bariums und seiner Verbindungen werden die Aufbereitungs- und Aufschlussverfahren, besonders des Schwerspats, beschrieben. Es folgen dann Angaben über die technischen Darstellungsmethoden für das Bariummetall und die wichtigsten Bariumsalze sowie deren Verwendung. Methoden zur Anreicherung und Abtrennung von Barium-Isotopen

sowie physiologische Eigenschaften (Toxicität) werden im Kapitel über die Darstellung des Elementes berücksichtigt. Der üblichen Einteilung entsprechend folgt dann eine Beschreibung der physikalischen Eigenschaften und des chemischen Verhaltens des Elementes bezw. Ions. Ungefähr die Hälfte des Bandes befasst sich mit den Verbindungen des Bariums, wobei zunächst die Legierungen mit Sb, Bi, Ca und Sr besprochen werden. Anschliessend werden die Verbindungen mit H, O, N, Halogen, S, besonders Bariumsulfat und Bariumcarbonat, sowie die Verbindungen mit B, C, Si, P, As, Sb, Bi, Be, Mg, Ca, Sr und Alkalimetallen behandelt. Den Schluss des Bandes bilden Angaben über die Herstellung und Eigenschaften von Erdalkalioxydkathoden, wozu der Inhalt von mehr als 300 Patentschriften ausgewertet wurde. Der Band ist mit Marginalien in englischer Sprache versehen und enthält ein deutsch–englisches Sachregister.

K. EDER (Genf)

Anal. Chim. Acta, 24 (1961) 393–394

Mises au point de chimie analytique pure et appliquée et d'analyse bromatologique, publiées sous la direction de J. A. GAUTIER, Septième série, un volume de 230 pages avec 48 figures et 9 planches dont 1 en couleur, format 16.5 × 25 cm, Masson et Cie., Paris, broché 48 NF.

Cet excellent ouvrage faisant partie d'une collection dont j'ai déjà, ici même, vanté les mérites, rassemble le texte de six conférences magistrales avec tableaux et bibliographie abondante. Il débute par un article sur la spectrographie d'émission dans l'ultra-violet par V. BRUSTIER ET G. PITET dans lequel ces auteurs donnent la pratique des procédés utilisés pour la recherche et le dosage d'éléments métalloïdiques et métalliques; ils indiquent ensuite les applications aux médicaments, aux substances d'origine biologique dans leurs rapports avec la toxicologie criminelle et industrielle. Le Professeur P. CORDIER étudie ensuite l'oxydation permanganique en analyse organique, dans le but de déterminer la nature des composés éthyléniques, la place de la double liaison, la migration de celle-ci; il expose aussi les hypothèses sur le mécanisme de cette oxydation. Dans un article très étendu et de caractère très moderne, J. KIGER expose les méthodes d'analyse des fibres textiles, naturelles, artificielles et synthétiques. M. MIOCQUE brosse ensuite un tableau d'ensemble relatif à l'analyse des composés acétyléniques qui ont acquis maintenant un développement industriel considérable. L'auteur ne se limite pas à l'analyse de l'acétylène. F. PELLERIN nous fait part, ensuite de nouvelles acquisitions en analyse organique fonctionnelle, notamment les analyses protométriques. Enfin, R. SAUNIER traite de l'analyse des produits sucrés industriels et commerciaux en présentant et critiquant les principales méthodes: saccharimétrie, densimétrie et réfractométrie.

L'ouvrage est agréablement présenté et se termine par un index des matières traitées dans les sept séries parues jusqu'ici et déjà, on nous annonce un programme très attrayant pour l'année 1961 . . .

CL. DUVAL (Paris)

Anal. Chim. Acta, 24 (1961) 394

Die quantitative Bestimmung der Alkaloide in Drogen und Drogenzubereitungen, by O.-E. SCHULZ AND F. ZYMALKOWSKI, *Die chemische Analyse*, Vol. 47, 295 pp. Ferdinand Enke Verlag, Stuttgart, 1960, Geheftet DM 73.—; Ganzleinen DM 77.—.

The introduction of modern procedures for the extraction, isolation, purification, separation, and determination of alkaloids in vegetable drugs has been the subject of numerous investigations in later years. An up-to-date summary of this subject, which is still of topical interest, would be of great value. The present book only partially satisfies this requirement. It is surprising to read, on page 1, the explanation of the properties of alkaloids as bases, and in particular an account of titration in non-aqueous media is quite out of date and completely ignores KOLTHOFF's theories.

The most valuable part of the book is the 2nd part; there are 26 sections in which are described numerous analytical methods for the same number of drugs. The choice of the methods appears to be a little haphazard. In some cases those who first introduced an analytical method are not mentioned, but only later authors; this applies *e.g.* to the polarographic determination of morphine. Various newer and significant works on partition chromatographic analysis and ion-exchange methods are omitted.

However, despite its discrepancies there is so much material collected together in this book that it will be useful for those laboratories which carry out alkaloidal analyses.

F. REIMERS (Copenhagen)

Anal. Chim. Acta, 24 (1961) 395

Gasanalyse, Methoden der Arbeitspraxis, von F. BAYER UND G. WAGNER, 3. umgearbeitete Auflage, *Die chemische Analyse*, Bd. 39, Verlag Enke, Stuttgart, 1960, 288 S., 116 Abb.

Die nun vorliegende 3. Auflage dieses Buches dürfte von vielen seit langem erwartet sein, zumal die zusammenfassende Literatur über das Gebiet der Gasanalyse im deutschsprachigen Schrifttum relativ spärlich ist. In der Anlage schliesst sich das Buch an die in der 2. Auflage gewählte und bewährte Art der Darstellung an. Das Buch ist in einen allgemeinen Teil (43 Seiten), in dem die Gasgesetze und allgemeine gasanalytische Apparaturen behandelt werden, und einen speziellen Teil gegliedert. In dem letzteren wird zunächst in 13 Unterabschnitten (130 Seiten) die Bestimmung der einzelnen Gase besprochen. Dann folgen Abschnitte über physikalische und chemisch-physikalische Methoden der technischen Gasanalyse (46 Seiten), über Bestimmungen von Gasen in festen Körpern (13 Seiten), über Spurenanalysen von Gasen (11 Seiten), über Bestimmung von Schwebestoffen (8 Seiten) und über physiologische Wirkungen von Gasen insbesondere unter gewerbehygienischen Gesichtspunkten (17 Seiten). In dem Bestreben, „die blosse Literaturzusammenstellung bewusst zurückzudrängen" und „mehr erprobte Verfahren" zu beschreiben, sind die Verfasser nach Ansicht des Referenten reichlich weit gegangen, denn unter den 263 Literaturzitaten zu den Seiten 1–173 findet man nur 12 Arbeiten, die nach 1940, dem Erscheinungsjahr

der 2. Auflage dieses Buches, erschienen sind (darunter sind nur 4, die nicht von den Verfassern des vorliegenden Buches oder von Fachkollegen ihres Heimatlandes stammen). Den modernen Verfahren der Gasanalyse ist verhältnismässig wenig Raum gewidmet. Bei dem Ansehen, das die Reihe *Die chemische Analyse* besitzt, in welcher das vorliegende Buch erschienen ist, muss man bedauern, dass eine Reihe äusserer Unschönheiten dem Gesamteindruck, den man bei sorgfältigem Lesen von diesem Buch gewinnt, abträglich ist. So ist die Nomenklatur nicht den heute gültigen Bestimmungen angepasst worden und auch innerhalb des Buches nicht einheitlich. Es ist wenig schön, wenn für einen Begriff bis zu sechs verschiedene Abkürzungen oder Bezeichnungen angewendet werden. Auch ist das Buch nicht frei von Verwechslungen, wodurch in einem Fall ein ganzer Abschnitt unverständlich wird und die Zahl der Druckfehler, zum Teil Stellenfehler in der Kommasetzung bei Zahlenangaben, scheint über das Mass des Üblichen hinauszugehen. Es bleibt zu wünschen, dass bei einer späteren Auflage einmal die neueren Arbeiten und die modernen Verfahren in stärkerem Umfang berücksichtigt werden und dass zum anderen grössere Sorgfalt auch im Hinblick auf Einzelheiten geübt wird. Dem kritischen Benutzer wird auch diese Auflage trotzdem von Nutzen sein.

H. Bode (Hannover)

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VIII. Colloquium Spectroscopium Internationale 1959 in Luzern, Gesamtausgabe der Vorträge und Referate, Herausgegeben von der Schweizerischen Arbeitsgemeinschaft für Spektralanalyse, Verlag H. R. Sauerländer & Co., Aarau (Schweiz), 317 S.

Der Band gibt einen Überblick über die neueren Forschungsergebnisse auf den verschiedenen Gebieten der Spektroskopie. Bei den etwa 70 Vorträgen, deren Inhalt ganz überwiegend in vollem Wortlaut wiedergegeben ist, ist es unmöglich, alle einzelnen Themen anzuführen, doch seien die Themen der als Übersichtsreferate gehaltenen Hauptvorträge genannt: Anwendung der optischen und der Radiospektroskopie auf die Untersuchung der interstellaren Materie, spektroskopische Diagnostik in der Physik heisser Plasmen, Betrachtungen über quantitative Flammenspektroskopie, Probleme der Massenspektroskopie und Mikrowellenspektroskopie. Die überwiegende Zahl der weiteren Vorträge befasst sich mit der Emissionsspektroskopie. Hierbei wird über apparative Fortschritte, Arbeitsmethoden zur Lösung von Einzelproblemen, bestimmte Arbeitstechniken und in einer grösseren Zahl von Vorträgen auch über Untersuchungen physikalischer und chemischer Vorgänge, die sich bei der Durchführung spektroskopischer Verfahren abspielen, berichtet.

Zwei weitere Vortragsgruppen befassen sich mit der Massenspektroskopie und der Röntgenfluoreszens-Spektroskopie. Zahlreiche graphische Darstellungen, Abbildungen und Tabellen machen die Angaben der Texte anschaulich.

Jeder, der daran interessiert is, mit der Entwicklung der spektralanalytischen Arbeitsverfahren Schritt zu halten, wird nicht darum herumkommen, sich eingehend mit dem Inhalte des hier vorliegenden Bandes auseinanderzusetzen.

H. Bode (Hannover)

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THE CHARACTERISATION AND DETERMINATION OF NITROGENOUS ORGANIC BASES IN MIXTURES WITH AMMONIUM REINECKATE

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Ammonium reineckate has been used for the isolation, characterisation and determination of nitrogenous organic bases. It has been applied to the following classes of substances: simple amines[1-3], amino acids[4-11], alkaloids[12-25], antibiotics from *streptomyces fradiae*[26-32], muscarine and related derivatives[33,34], proteins[35], quaternary ammonium compounds[36-38], synthetic bases such as narcotics[23,39,40], antihistamines[17,23], sulphonamides[23], anaesthetics[41], and many other organic bases[42-48]. It has also been used for the spectrophotometric determination of the molecular weights of these compounds[23,49].

In spite of the extensive usage of this reagent, it has not yet been utilised systematically to characterise and determine organic bases in mixtures. STRACK AND SCHWANEBURG[50] reported the separation of choline from betaine obtained from animal tissues using this reagent in 1936. The potentialities of ammonium reineckate as a reagent for the separation of organic bases has not been further investigated and it is the object of the present investigation to evaluate the usefulness of ammonium reineckate for this purpose. This must necessarily involve the study of the reaction mechanism between ammonium reineckate and organic bases, a study which should be of considerable value because of the importance of the reaction to the analyst as well as the toxicologist. A preliminary report on this investigation has already been published[51].

EXPERIMENTAL

Formation of reineckates in alkaline media

About 50 mg of a base was added to 50 ml of water and a few drops of ammonia ($d = 0.88$) followed by 30 ml of ammonium reineckate. The precipitate obtained was filtered, dried and recrystallised from 60% ethanol. Piperidine, dimethylamine, trimethylamine, diethylamine and choline gave the expected reineckates when reacted under these conditions. However with pyridine, aniline and caffeine, no reineckates were obtained.

Effects of variation of pH on yields of reineckates of water-soluble bases

Buffered solutions of pH 1 to 12 were prepared according to CLARK AND LUB[52,53].

Ammonium reineckate solution — approximately 3% solution prepared by dis-

solving 3 g of ammonium reineckate in 100 ml of cold water and filtering through a Whatman No. 1 filter paper and then through a Whatman No. 42 paper. Freshly prepared solutions were used in all these experiments. The bases used were piperidine, pyridine, morpholine, caffeine and nicotine.

Procedure. About 25 mg of the base was added to 30 ml of the buffer solution of the appropriate pH followed by 15 ml of ammonium reineckate solution. The resulting solution was cooled in a refrigerator for 2 h and filtered through a sintered glass crucible with suction. The precipitate was washed with 5 ml of the appropriate buffered solution and then dissolved in acetone. The acetone solution was transferred to a 25-ml volumetric flask, made up to volume and the optical density of the solution was measured at 525 mμ with a Hilger spectrophotometer. The amount of base recovered was calculated by means of the following equation:

$$w = A/\varepsilon \cdot M \cdot 25/1000 \qquad (1)$$

where w = weight of base recovered in mg, A = observed optical density, ε = gram-molecular extinction coefficient of ammonium reineckate, ($\varepsilon_{525\ m\mu} = 106.5$), and M = molecular weight of the base used in g. The derivation of this formula has already been discussed[23].

For nicotine the precipitate obtained was filtered, dried over phosphorus pentoxide and weighed. Table I shows the recoveries and compositions of the nicotine reineckates

TABLE I

RECOVERY OF NICOTINE AS REINECKATE AT VARIOUS pH

No.	*Nicotine mg*	*pH*	*Reineckate obtained mg*	*Cr content of reineckate*
1	50	2	246.2	12.92
2	50	2	247.2	12.89
3	50	3	245.8	12.91
4	50	3	246.0	12.86
5	50	4	234.2	12.46
6	50	4	232.5	12.41
7	50	5	177.0	11.24
8	50	5	178.5	11.36
9	50	6	177.0	11.31
10	50	6	177.0	11.25
11	50	7	178.3	11.07
12	50	7	178.6	11.13
13	50	8	150.1	10.97
14	50	8	149.5	10.85
15	50	9	148.5	10.86
16	50	9	148.6	10.77
17	50	11	127.3	10.83
18	50	11	136.2	10.72
19	50	11	121.5	10.69

Theoretical yield for 50 mg of nicotine as the mono-reineckate is 148.3 mg, Cr = 10.81%, and as the di-reineckate is 247.0 mg ,Cr = 12.97%.

obtained. Fig. 1 shows the recoveries for piperidine, pyridine, morpholine and caffeine at various pH.

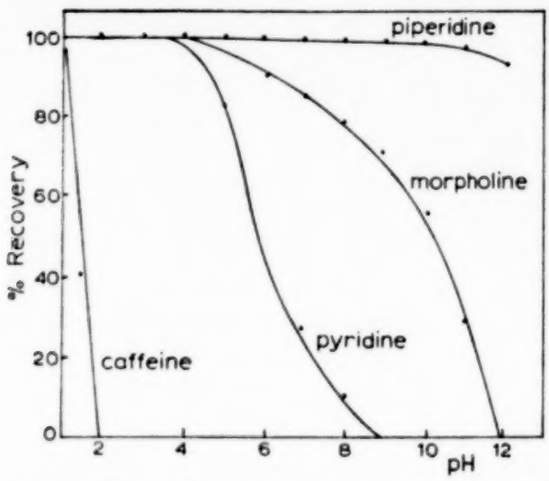

Fig. 1. Recoveries of bases as reineckates at various pH.

Preparation of barium reineckate

A saturated solution of Reinecke's acid (prepared by precipitation from a saturated solution of ammonium reineckate with concentrated hydrochloric acid) was added to a saturated solution of barium chloride. The barium reineckate obtained was recrystallised by dissolution in a minimum quantity of methanol and reprecipitation by the addition of excess of ether. The pure barium reineckate was obtained after two recrystallisations.

	Calcd. for $Ba[Cr(NH_3)_2(SCN)_4]_2$ %	*Found* %
Barium	17.72	17.68
Nitrogen	21.78	21.85

Reaction between barium reineckate and bases in absolute alcoholic solutions

The A.R. ethanol and isopropanol used in these experiments were twice distilled over sodium.

TABLE II

RECOVERIES OF PIPERIDINE AND MORPHOLINE AS THEIR REINECKATES FROM REACTION IN ABSOLUTE ALCOHOLS

Amine	*Amount used mg*	*Ethanol Reineckate obtained mg*	*Cr %*	*Amount used mg*	*Iso-propanol Reineckate obtained mg*	*Cr %*
Piperidine	48.1	204.0	12.75	44.2	207.3	12.93
	43.2	201.3	12.81	43.1	199.2	12.84
Morpholine	53.1	143.2	12.82	57.2	149.2	12.91
	47.2	140.1	12.71	51.0	155.0	12.84

About 200 mg of recrystallised barium reineckate was dissolved in 30 ml of the absolute alcohol and approximately 50 mg of the base was then added. The solution was allowed to stand at room temperature for 3 h, and the precipitate was filtered, dried over phosphorus pentoxide and weighed. The results obtained were shown in Table II. Aniline (pK_b 9.3) and pyridine (pK_b 8.6) gave no precipitates under these conditions.

Formation of reineckates of weak bases

A. Preparation of reineckates of water-soluble bases. About 2 g of the base was dissolved in 20 ml of water and 5 ml of concentrated hydrochloric acid was added to this solution followed by 80 ml of 2% ammonium reineckate solution. The precipitate which was obtained was filtered and recrystallised with 0.1 *N* hydrochloric acid. To prepare urea reineckate 8 g of urea was used. The reineckates of urea, thiourea, acetamide and acetone semicarbazone were prepared in this manner.

B. Preparation of piperine reineckate. About 300 mg of the piperine was dissolved in 15 ml of chloroform in a separating funnel. To this were added 10 ml of 25% hydrochloric acid solution and 80 ml of 2% ammonium reineckate solution. The resulting mixture was shaken thoroughly and the reineckate salt formed was filtered and recrystallised in a minimum quantity of ethanol which was subsequently diluted with 0.1 *N* hydrochloric acid. The dried reineckate salt is yellow but gives a red coloured solution in acetone.

C. Preparation of diphenylamine reineckate. About 200 mg of diphenylamine was dissolved in approximately 5 ml of concentrated sulphuric acid. Approximately 15 ml of water was added slowly to this solution. After cooling the solution, 80 ml of ammonium reineckate was added. The diphenylamine reineckate obtained was recrystallised as described earlier.

Preparation of di-reineckates of nicotine, quinine and thiamine

Procedure 1. Formation in acid media. About 100 mg of the base or its salt was dissolved in 20 ml of *N* hydrochloric acid solution. Excess of ammonium reineckate solution was added and the precipitate formed was filtered and recrystallised by dissolving the precipitate in the minimum quantity of acetone and subsequently diluting this acetone solution with *N* hydrochloric acid. Analyses of the chromium contents of the compounds so obtained showed them to be the di-reineckates of these bases.

Procedure 2. Conversion of mono-reineckates to di-reineckates. An acetone solution of mono-reineckate was added to a solution of ammonium reineckate acidified with *N* hydrochloric acid. On chilling the di-reineckates were obtained.

Preparation of mono-reineckates of nicotine, quinine and thiamine

Procedure 1. Formation in alkaline media. About 100 mg of nicotine, quinine sulphate or thiamine hydrochloride was added to a buffer solution of pH 8.5, followed by 50 ml of ammonium reineckate solution which was added with stirring. The mono-reineckates of these compounds which were obtained after chilling were filtered and recrystallised from 50% acetone solution.

Procedure 2. Conversion of di-reineckates to mono-reineckates. To an acetone solution of the di-reineckate were added two drops of 10% ammonia and excess distilled water. The precipitate obtained was filtered and recrystallised from 50% acetone solution. Pure mono-reineckates of these three compounds were obtained by these two procedures.

Separation of piperidine and pyridine

Weighed quantities of piperidine and pyridine were dissolved in 60 ml of buffer solution of pH 9. To this solution was added 30 ml of ammonium reineckate solution. After cooling for one hour the solution was filtered through a weighed sintered glass crucible under suction. The piperidine reineckate was washed with a few ml of buffered solution, dried over phosphorus pentoxide and weighed.

During the filtration of piperidine reineckate an acid trap containing a few ml of dilute sulphuric acid was used to trap any pyridine that may have volatilised from the filtrate during suction. This sulphuric acid was added to the filtrate which was further acidified with 50% sulphuric acid.

Pyridine was precipitated as the reineckate, filtered and weighed as described above. The recoveries of the bases are shown in Table III.

TABLE III

RECOVERIES OF BASES FROM MIXTURES

No.	*Mixtures*	*Amount added mg*		*Amount recovered mg*	
1	Piperidine–Pyridine	83	147.3	82.6	145.0
2	Piperidine–Pyridine	150.8	38.7	151.2	37.3
3	Piperidine–Pyridine	23.4	15.8	21.9	16.3
4	Codeine–Caffeine	52.4	256.3	51.4	252.7
5	Codeine–Caffeine	21.4	84.3	20.1	80.6
6	Codeine–Caffeine	15.7	482.4	15.2	477.5
7	Codeine–Caffeine	20.2	90.4	18.7	87.7

Separation of codeine and caffeine

Weighed amounts of codeine phosphate and caffeine were dissolved in 40 ml of buffer solution of pH 3.5 with warming. After cooling, 15 ml of ammonium reineckate solution was added, and the solution was cooled to 0° for one hour and filtered. The codeine reineckate was dissolved in acetone and determined colorimetrically by measuring the optical density of the solution at 525 mμ. The filtrate containing the caffeine was made alkaline with sodium hydroxide solution and extracted with chloroform. Evaporation of the chloroform yielded the caffeine which was dried and weighed.

Determination of mixtures of mono- and di-basic compounds

1. Determination of nicotine and pyridine in mixtures. To a 100-ml beaker were added 10 ml of a solution containing nicotine and pyridine, 30 ml of buffer solution of pH 8.5, and 15 ml of ammonium reineckate solution. After chilling for 2 h the solution was filtered through a sintered glass crucible under suction. The precipitated nicotine

mono-reineckate was washed with 3 to 5 ml of the buffer solution and dissolved in acetone and 2 ml of 0.1 N hydrochloric acid, and the solution was transferred to a V_0 ml volumetric flask and diluted to mark. The absorption (A_0) of this solution was measured at 525 mμ. The amount of nicotine recovered was calculated from the following formula:

$$w_0 = A_0/106.5 \cdot M_0 \cdot V_0/1000 \qquad (2)$$

where w_0 = weight of nicotine recovered in mg, 106.5 = gram-molecular extinction coefficient of ammonium reineckate in acetone at 525 mμ and M_0 = molecular weight of nicotine in g.

To ascertain the pyridine content of the mixture another 10 ml of the solution was added to 20 ml of N hydrochloric acid solution followed by 25 ml of ammonium reineckate solution. The precipitated nicotine di-reineckate and pyridine reineckate were filtered through a sintered glass crucible, dissolved in acetone, transferred to a volumetric flask of V ml and diluted to mark. The optical density of this solution (A) at 525 mμ was measured and the pyridine content calculated from the following equation:

$$w = (AV/V_0 - 2A_0)/106.5 \cdot M \cdot V/1000 \qquad (3)$$

where w = amount of pyridine recovered in mg, M = molecular weight of pyridine in g. The recoveries are shown in Table IV.

TABLE IV

DETERMINATION OF MIXTURES OF MONO- AND DIBASIC COMPOUNDS

No.	*Mixtures*	*Amounts added mg*		*Optical densities*		*Amounts recovered mg*	
				A_0	A		
1	Nicotine–Pyridine	10	10	0.250	1.063	9.52	10.43
2	Nicotine–Pyridine	10	10	0.252	1.060	9.55	10.33
3	Nicotine–Pyridine	10	10	0.264	1.071	10.02	10.05
4	Nicotine–Piperidine	10	10	0.776	1.039	10.00	10.03
5	Nicotine–Piperidine	10	10	0.768	1.027	9.85	10.01
6	Nicotine–Piperidine	10	10	0.757	1.030	10.40	9.70
7	Thiamine HCl–Choline	15	10	0.536	0.738	16.00	9.50
8	Thiamine HCl–Choline	15	10	0.530	0.722	15.10	9.60

Volume of acetone used $V_0 = V = 25$ ml in the above experiments

2. Determination of nicotine and piperidine. The procedures for the determination of piperidine and nicotine in mixtures were identical to those described earlier. However, at pH 8.5 both nicotine mono-reineckate and piperidine reineckate were formed and in acid media the nicotine di-reineckate and piperidine reineckate were formed.

Hence the nicotine and piperidine contents can be calculated from the following formulae:

$$w_0 = (AV/V_0 - A_0)/106.5 \cdot M_0 \cdot V_0/1000 \quad (4)$$

$$w = [AV/V_0 - 2\{(AV/V_0) - A_0\}] / 106.5 \cdot M \cdot V/1000 \quad (5)$$

where w_0 = amount of nicotine recovered in mg, A_0 = optical density of acetone solution of nicotine mono-reineckate and piperidine reineckate at 525 mμ, M_0 = molecular weight of nicotine in g, V_0 = volume of acetone used to dissolve the nicotine mono-reineckate and piperidine reineckate, w = amount of piperidine recovered, A = optical density of acetone solution of nicotine di-reineckate and piperidine reineckate, M = molecular weight of piperidine in g, and V = volume of acetone used to dissolve the nicotine di-reineckate and piperidine reineckate.

Mixtures of thiamine hydrochloride, a di-basic compound and choline, a strongly basic quaternary compound were also determined by the procedures described above and the recoveries are also shown in Table IV.

The isolation of strychnine from highly decomposed cadavers

About 300 g of human liver from an authenticated case of strychnine poisoning was left to stand at room temperature for one week after which it was finely cut, treated with 10% tartaric acid and extracted with 75% ethanol with warming. The alcoholic solution was filtered and the filtrate evaporated. This residue was taken up with 75% alcohol, filtered and again evaporated. The residue was dissolved in water acidified with 0.1 N hydrochloric acid, filtered and extracted with ether to remove any acidic or neutral materials that might be present. The aqueous layer was made ammoniacal, transferred to a separating funnel and extracted with chloroform. The ammoniacal aqueous layer was kept for later treatment.

To the combined chloroform extracts were added 20 ml of buffer solution of pH 11 and 5 ml of ammonium reineckate solution. Some insoluble reineckates were formed at the interface between the water and the chloroform layers. The chloroform layer was separated and washed with water. Half of the chloroform extracts was evaporated and subjected to the usual colour and crystal tests. The remaining chloroform was extracted with 0.1 N hydrochloric acid. This acid solution was made alkaline and extracted with chloroform. The chloroform was evaporated and the residue was dissolved in 95% ethanol. The spectral curve of this ethanolic solution is shown in Fig. 2 and is identical to that of pure strychnine.

Ammonium reineckate solution was added to the ammoniacal aqueous layer from above and more precipitate was obtained. The precipitate was recrystallised from aqueous acetone mixture; its molecular weight was determined spectrophotometrically[23] and was found to average 78. This indicates that the isolated bases were mostly ptomaines and not any of the common alkaloids since the latter have molecular weights which are generally greater than 150.

DISCUSSION OF RESULTS

Reaction mechanism

The formation of the reineckates has been hitherto carried out in acidic aqueous

media and the reaction between amine salts and ammonium reineckate has been postulated to proceed according to the following equation[1,39]:

$$B \cdot HX + NH_4[Cr(NH_3)_2(SCN)_4] \rightarrow NH_4X + BH \cdot [Cr(NH_3)_2(SCN)_4] \quad (6)$$

This equation however is applicable to reactions between amine salts and ammonium reineckate only and does not explain some of the reactions between certain free bases and ammonium reineckate in aqueous alkaline media. It has been observed that certain bases form reineckates in alkaline media while others do not. A closer study of the properties of the bases which react with ammonium reineckate in alkali media revealed that they are strongly basic substances such as piperidine (pK_b 2.8), diethylamine (pK_b 2.5), trimethylamine (pK_b 3.2) and quaternary ammonium compounds such as choline. Dibasic substances formed the di-reineckates in acid media and in alkaline media yielded the mono derivatives. Furthermore, Fig. 1 shows that the yields of the reineckates depend on the pK_b values of the bases as well as on the pH of the reaction media.

These observations suggest that the formation of the reineckate proceeds according to the following pattern. When a basic substance (B) is dissolved in water the following equilibrium exists:

$$B + H_2O \rightleftharpoons BH^+ + OH^- \quad (7)$$

With the addition of an ammonium reineckate solution the conjugate acid BH^+ thus formed reacts with the $[Cr(NH_3)_2(SCN)_4]^-$ ions arising from the dissociation of ammonium reineckate, and the relatively insoluble complex is formed:

$$BH^+ + [Cr(NH_3)_2(SCN)_4]^- \rightarrow BH[Cr(NH_3)_2(SCN)_4] \quad (8)$$

The removal of the conjugate acid BH^+ as the insoluble reineckate disturbs the equilibrium represented by eqn. (7) and more conjugate acid is then formed to replace that removed. It is obvious therefore that in an aqueous solution the formation of the reineckate complex depends on the formation of the conjugate acid BH^+ from the base B.

The extent to which the equilibrium as represented by eqn. (7) exists, depends on the strengths of the bases as well as on the pH of the reaction media, and the equilibrium constant is given by

$$K_b = [OH^-] \cdot [BH^+]/[B] \quad (9)$$

In logarithmic notation eqn. (9) becomes

$$\log [B]/[BH^+] = pK_b + pH - 14 \quad (10)$$

The reaction between ammonium reineckate and quaternary ammonium compounds as choline is one of substitution thus

$$R_4N \cdot X + NH_4[Cr(NH_3)_2(SCN)_4] \rightarrow RN \cdot [Cr(NH_3)_2(SCN)_4] + NH_4X \quad (11)$$

and this reaction is independent of the pH of the reaction media. This is true with

choline which forms a reineckate even in a 5% sodium hydroxide solution. The reaction in strongly alkaline media is not recommended because the ammonium reineckate decomposes rapidly under these conditions.

Reaction between bases and barium reineckate in absolute alcoholic solutions

Since alcohols possess protogenic properties[54] the base-alcohol equilibrium is

$$B + ROH \rightleftharpoons BH^+ + RO^- \qquad (12)$$

From a study of the reineckate formation of piperidine, morpholine, pyridine and aniline it was found that equilibrium (12) is dependent on the pK_b values of the base present. With strong bases such as piperidine and morpholine the equilibrium proceeds almost completely to the right. With weak bases such as pyridine and aniline the equilibrium lies to the left.

Since the formation of reineckates under these conditions is dependent on the pK_b values of the bases this procedure can be used for the separation of bases. Ammonium reineckate can be used in place of barium reineckate.

Separation of bases with ammonium reineckate

Eqn. (10) predicts the possibility of using ammonium reineckate for the separation of organic bases by varying the pH of the reaction media to values which will be favourable or unfavourable for the formation of a particular reineckate if the pK_b values of the compounds are known. Since the formation of the reineckates depends entirely on the formation of the conjugate acid BH^+ the ideal condition would be to have the term $\log [B]/[BH^+]$ in eqn. (10) equal to a negative value, although a value of +1 may be permissible depending on the solubility of the particular reineckate derivative formed. A clearer picture of the reaction can be obtained by considering the specific cases of piperidine (pK_b 2.8) and pyridine (pK_b 8.6) at pH 9. In the case of piperidine at pH 9

$$\log [B]/[BH^+] = 2.8 + 9 - 14 = -2.2$$

$$\log [B]/[BH^+] = 3.8$$

that is

$$[B]/[BH^+] = 6.3/1000$$

This shows that more than 99.4% of the piperidine exists as the conjugate acid BH^+ and hence the possible formation of piperidine reineckate in alkaline media of pH 9.

Similarly, it can be shown that at pH 9 about 99.7% of the pyridine exists as the free base B, hence pyridine fails to form a reineckate at this pH. However, at pH 2 more than 99.9% of the pyridine exists as the conjugate acid BH^+ which explains the formation of pyridine reineckate in acid media.

Satisfactory recoveries were obtained for the determination of mixtures of (*a*) pyridine and piperidine and (*b*) codeine and caffeine as shown in Table III where the bases were isolated and determined. With mixtures such as (*a*) nicotine and pyridine, (*b*) nicotine and piperidine and (*c*) thiamine hydrochloride and choline, the bases were not isolated but conditions could be chosen which favoured the formation of the mono- or di-reineckates of the dibasic substances, thus making it possible to estimate bases in such mixtures. The recoveries for such mixtures are shown in Table IV.

Eqns. (2) and (3) are of general application for the determination of mixtures of a dibasic compound and a moderately weak monobasic compound, whilst eqns. (4) and (5) can be applied to the determination of mixtures of a dibasic substance and a strong monobasic compound.

Formation of mono- and di-reineckates of dibasic substances

With a knowledge of the reaction mechanism it is possible to control the conditions for the formation of mono- or di-reineckates of dibasic compounds. The dibasic substances can be treated as a mixture of two bases with different pK_b values and the mono- or di-reineckates of nicotine (pK_{b1} 6.2, pK_{b2} 10.9), quinine (pK_{b1} 6.0, pK_{b2} 9.7) and thiamine hydrochloride had been successfully prepared by varying the pH of the reaction media. With dibasic compounds the nature of the reineckates formed depends on the pH of the reaction media. At certain pH values, mixtures of mono- and di-reineckates of nicotine were obtained (Table I). It is important therefore to form the derivatives under the proper pH conditions, otherwise the results obtained can be very misleading.

Although the formation of mono- and di-reineckates of nicotine, quinine and thiamine hydrochloride is reversible, that is

$$\text{mono-reineckate} \underset{\text{alkaline}}{\overset{\text{acid}}{\rightleftharpoons}} \text{di-reineckate}$$

this is not generally true with reineckates of other dibasic compounds. The di-reineckates of many antihistamines yielded the mono-reineckates when recrystallised from

TABLE V

REINECKATES OF BASES

Reineckates	*Decomp. temp. uncorr.* °C	*Cr content*	
		Calc. %	*Found* %
Quinine (mono)	145–149	8.09	8.21
Quinine (di)	216	10.82	10.90
Thiamine (mono)	148–149	8.93	8.96
Thiamine (di)	160–162	11.51	11.51
Nicotine (mono)	184–185	10.81	10.92
Nicotine (di)	160–162	12.97	12.81
Piperidine	198–202	12.90	12.84
Morpholine	175–177	12.80	12.91
Pyridine	198–202	13.02	13.16
Caffeine	137	10.10	9.93
Diethylamine	260–262	13.24	13.21
Dimethylamine	273–274	14.25	14.36
Triethylamine	200–207	12.35	12.43
Diphenylamine	146–149	10.65	10.70
Acetone semicarbazone	136–140	11.71	11.36
Acetamide	136–138	13.75	13.52
Thiourea	138–140	13.16	13.07
Urea	121–122	13.75	12.35 12.51
Piperine	147–149	8.63	6.81 6.55

60% ethanol and no di-reineckates could be obtained from their mono-reineckates. This was attributed to the instability of these di-reineckates to heat and ethanol[23].

Preparation of reineckates of weak bases

Very weak bases such as urea (pK_b 13.8), piperine (pK_b 8.8) and diphenylamine have been reported not to form any reineckates[1] but eqn. (10) suggested that reineckates of these bases should be obtainable if the reaction were carried out at a very low pH. The reineckates of these three substances, together with those of thiourea, acetamide and acetone semicarbazone, were then prepared by this procedure. The chromium contents of the reineckates agreed with the theoretical values with the exceptions of urea and piperine reineckates (Table V). The low chromium contents of these reineckates are being further investigated.

Isolation of strychnine from highly decomposed cadavers

One of the main problems which confronts every toxicologist is the separation of poisons from putrified organs. Many of the substances produced during putrefaction of cadavers resemble alkaloids in their reactions towards general reagents and certain ptomaines resemble well-defined alkaloids even with special reagents[55]. BRIEGER[56] has described a method for the isolation of certain ptomaines from human cadavers using an alcoholic mercuric chloride solution as the precipitating reagent, but it is obvious that this reagent cannot be used in toxicology for the same purpose, because mercuric chloride will also precipitate many of the wanted alkaloids. The isolation of strychnine from highly putrified human livers using the proposed procedure gave satisfactory results and the high purity of the isolated alkaloid is demonstrated by the spectra shown in Fig. 2.

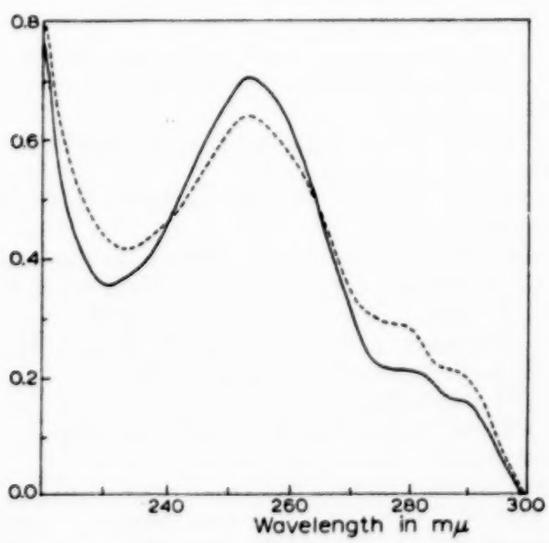

Fig. 2. Spectra of strychnine. ———, the pure strychnine, 2 mg/100 ml -----, from liver. Solvent, 95% ethanol.

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SUMMARY

The reaction between nitrogenous organic bases and ammonium reineckate was studied and was found to depend on the basicity of the bases and the pH of the reaction media. An expression is given which relates the dissociation constant pK_b of a base and the pH of the reaction; when the pK_b of a base is known the pH required for the complex formation can be calculated. The conditions for the formation of reineckates of very weak bases together with the formation of mono- and di-reineckates of dibasic substances are given. The separation of bases whose pK_b values are sufficiently far apart and the determination of mixtures of mono- and dibasic substances were effected by pH adjustment of the reaction media. The isolation of strychnine from putrified human livers is also described.

RÉSUMÉ

L'auteur a effectué une étude sur l'identification et le dosage des bases organiques azotées, en utilisant comme réactif le reinéckate d'ammonium. Quelques séparations sont décrites. Une méthode est également proposée pour l'extraction de la strychnine de cadavres, dans des cas d'empoisonnement.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Trennung und Bestimmung organischer Stickstoffhaltiger Basen mit Reinecke Salz sowie über die Isolierung von Strychnin aus der Leber stark verwester menschlicher Leichen.

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OPTIMUM "COOLING TIME" TO MINIMIZE INTERFERING ACTIVITY IN NON-DESTRUCTIVE ACTIVATION ANALYSIS

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INTRODUCTION

In quantitative non-destructive analysis for an element by neutron irradiation followed by γ-ray spectrometry, the error and detection limit depend on interfering γ-rays to a great extent. As a means of reducing the interference, a choice of a proper length of "cooling time" can be considered. Therefore, the relation between cooling time and the extent of interference has been examined theoretically. In this study, for convenience, the γ-ray of unit energy emitted from a nuclide formed (neutron-induced nuclide) to be determined*, is likened to a "signal", and the interfering γ-ray to a "noise". Thus, the purpose of the work was to discover how to choose a cooling time to make the "signal-to-noise ratio" large. The signal-to-noise ratio under consideration is in the adequately restricted range of γ-energy.

The case when the signal-to-noise ratio is varied by the choice of cooling time is, of course, limited to the case when the half-life of an interfering nuclide is different from that of the nuclide to be determined.

DERIVATION AND RESULTS

In any radionuclide formed the ratio of the emission rate of a γ-ray to the amount of the element which includes the parent of the radionuclide is given by

$$\frac{A_p^\gamma}{W} = N_A f \frac{\sigma_{ac} K}{M} \gamma_p \{1 - e^{-(\ln 2)t/T}\} e^{-(\ln 2)\theta/T}$$

where

A_p^γ = emission rate for an unconverted γ-ray (sec^{-1}),
W = the weight present of the element (g),
N_A = Avogadro's number,
f = flux density of neutrons ($cm^{-2}\,sec^{-1}$),
σ_{ac} = isotopic cross section for the neutron activation of a naturally-occurring, parent nuclide, *i.e.*, target isotope (cm^2),
K = fractional abundance of the parent nuclide,
M = chemical atomic weight of the element,
γ_p = fractional abundance of an unconverted γ-ray,
t = irradiation time (sec),
T = half-life of the nuclide formed (sec),
θ = time elapsed after irradiation, *i.e.*, the "cooling time" (sec).

* The determination of the nuclide formed leads to the determination of the element which is, in most cases, the final purpose in activation analysis.

(Eqn. (1) can be obtained by substituting the quantity $(\ln 2)/T$ for λ in the equation given by BOYD[1] and eliminating the quantities t', A_t' and A_∞ in the resultant equation by putting $t' = \theta$, $A_t' = A_p^\gamma/\gamma_p$, and $A_\infty = N_A f W \sigma_{ac} K/M$).

For convenience it is assumed that the probability for the appearance of one interfering nuclide is equal to the probability for the appearance of another interfering nuclide, and that the counting time is set sufficiently short compared with the cooling time.

Since the species of an interfering nuclide cannot usually be foreseen, the amount of $(\sigma_{ac}K/M)\gamma_p$ in eqn. (1) cannot be forecast for the interfering nuclide. In this situation the only method to be adopted is to adjust the amount of the latter part of eqn. (1):

$$\{1 - e^{-(\ln 2)t/T}\}\, e^{-(\ln 2)\theta/T} \qquad (2)$$

By inserting a suitably chosen value for θ the value of formula (2) may be made smaller for any interfering nuclide than for the nuclide to be determined. Such a value of θ, which is, so to speak, an optimum cooling time, can be expressed in terms of irradiation time, as can be deduced from formula (2), and therefore, it is necessary that both irradiation time, t, and cooling time, θ, are chosen properly. In order to compare the various combination of t and θ with each other, the amount of formula (2) has been plotted against T on log-log paper and Fig. 1 has been obtained. From Fig. 1

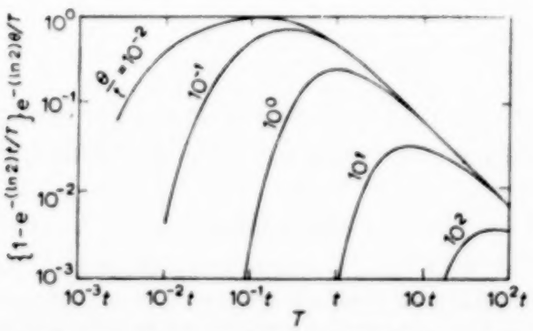

Fig. 1. $\{1 - e^{-(\ln 2)t/T}\}\, e^{-(\ln 2)\theta/T}$ *vs.* T.

it is deduced that for a certain half-life there is an optimum cooling time corresponding to an arbitrarily chosen irradiation time, since all the curves in Fig. 1 have points of one maximum. To obtain the optimum cooling time, formula (2) has been put as y and equation $dy/dT = 0$ has been solved. The result is

$$\theta_0 = \frac{t}{e^{(\ln 2)t/T_0} - 1} \qquad (3)$$

where θ_0 is the optimum cooling time, and T_0 is the half-life of a nuclide formed to be determined. According to eqn. (3), θ_0/T_0 has been plotted against t/T_0 on a log–log paper (Fig. 2). The optimum cooling time corresponding to an irradiation time can be readily found by the use of Fig. 2. For example, in activation analysis for hafnium by the formation of hafnium-179 *m* (19 sec), if the irradiation time is set at 60 sec,

t/T_0 becomes 60/19. Hence θ_0/T_0 is read in Fig. 2 as 0.40. Accordingly, θ_0 becomes $19 \cdot 0.40 = 7.6$ sec.

Moreover, from Fig. 1 it is seen that, when θ/t is less than 10°, the smaller is θ/t the smaller is the curvature at the maximum point; accordingly, selectivity for the

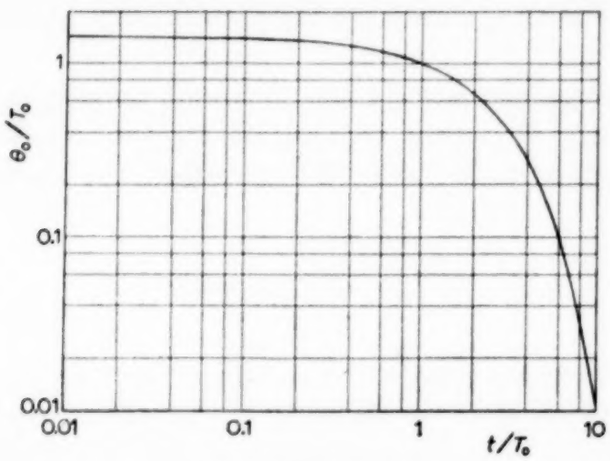

Fig. 2. θ_0/T_0 *vs.* t/T_0

signal becomes smaller when the half-life corresponding to the maximum point is looked upon as the half-life of the nuclide to be determined, and so the signal-to-noise ratio becomes smaller. It can also be seen that, when θ/t is larger than 10°, the curvature at the maximum is almost constant and larger than the ratio in the first case.

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SUMMARY

In order to choose the best "cooling time" to minimize interfering γ-rays in activation analysis, the "cooling time" has been examined theoretically. There is an optimum cooling time which depends on the time of irradiation and on the half-life of nuclide formed to be determined.

RÉSUMÉ

Après avoir effectué une étude sur le "temps de refroidissement" optimum, dans l'analyse par activation, l'auteur arrive à la conclusion que ce temps optimum dépend de la durée de l'irradiation et de la période du radio-isotope à doser.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über Beziehungen zwischen maximaler Kühlperiode und Störungen durch γ-Strahlen bei Analysen durch Aktivierung. Es wurde festgestellt, dass die maximale Kühlperiode von der Dauer der Bestrahlung und der Halbwertszeit des Isotopes abhängt.

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THE COMPOSITION OF RHODAMINE B CHLOROGALLATE

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Rhodamine B combines, in strong hydrochloric acid solution (6–8 *N*), with the chloro-acids of a number of metals to yield intensely coloured red or violet complexes. The complexes formed with Ga^{+3}, Au^{+3}, and Sb^{+5} are soluble in certain organic solvents, such as benzene and chlorobenzene, and have been used as a basis for sensitive photometric procedures for the determination of these elements[1]. Except in the case of antimony[2] no attempt seems to have been made to determine their constitutions. We have found that the gallium complex, in the organic phase, is represented by the formula $(RH)GaCl_4$ (R = rhodamine B). This confirms the formula $(RH)MCl_4$ (M = trivalent metal) suggested by ONISHI AND SANDELL[3] for the complexes of the trivalent elements.

EXPERIMENTAL

Determination of gallium : rhodamine B ratio

Caesium gallium sulphate (10 μg Ga^{+3}) dissolved in 5 ml of 6.5 *N* hydrochloric acid containing 1% w/v titanous chloride was treated with 0.5 ml of a 0.5% aqueous solution of rhodamine B. The gallium was quantitatively extracted by shaking with 8 ml of a 25% v/v solution of carbon tetrachloride in chlorobenzene[4]. After filtration through a glass wool plug, the organic phase was evaporated at 90°. The residue, which consisted of rhodamine B chlorogallate, was treated with water and diluted to 25 ml. Rhodamine B liberated by hydrolysis of the complex was determined by measurement of the optical density of the solution at 555 mμ in a 1-cm cuvette. Quadruplicate experiments gave optical densities of 0.403, 0.405, 0.406, 0.406, average 0.405. Blank runs were also carried out omitting the gallium (optical densities 0.007, 0.009, 0.010, average 0.009). The procedure was calibrated by evaporating to dryness 8-ml aliquots of a solution of purified rhodamine B (10.0 mg/l) in a 1 : 3 mixture of chloroform and chlorobenzene; the residues were diluted to 25 ml with water and gave optical densities of 0.466, and 0.467. These results lead to the ratio of 69.7 μg Ga : 472.8 μg $C_{28}H_{31}O_3N_2Cl$, *i.e.* 1 atom Ga ≡ 0.987 mole rhodamine B.

Attempts were made to recover rhodamine B directly from the organic phase by extraction with water or dilute sodium hydroxide, but although the organic phase turned colourless, no colour was formed in the aqueous phase.

* This work was carried out in partial fulfillment of the requirements for the degree of Ph.D. (London).

Determination of gallium : chlorine ratio

A solution of rhodamine B chlorogallate in 8 ml of carbon tetrachloride–chlorobenzene mixture was prepared as described above using 20 μg Ga^{+3}. The solvent was evaporated at room temperature in a small basin which was then allowed to stand overnight in vacuo over solid sodium hydroxide. The residue was dissolved in 1 ml of water and transferred to the outer chamber of a Conway microdiffusion cell, the inner compartment of which contained 1 ml of 20% w/v potassium iodide solution. A further 1 ml of water was used for washing the basin. Sulphuric acid (1 ml of 50% v/v) and *ca.* 0.2 g of potassium permanganate were added to the outer chamber. The cell was immediately sealed with a ground glass plate smeared with a mixture of medicinal paraffin and paraffin wax. Chlorine formed by oxidation of the chlorogallate complex was allowed to diffuse into the iodide solution for 6 h. The liberated iodine was titrated with 0.009 *N* thiosulphate from a micrometer syringe burette. The end-point was detected photometrically using starch as indicator. A blank experiment was run through the whole procedure without the addition of gallium. For standardisation, 2-ml aliquots of a standard sodium chloride solution containing 17.75 mg Cl^-/l were treated with permanganate and acid and diffused in the same manner. It was found that 69.7 μg of Ga was equivalent to 129, 134, 146, average 136 μg Cl $\equiv$ 3.8 μg-at.Cl. Hence in rhodamine B chlorogallate the Ga : Cl ratio is 1 : 4.

SUMMARY

The formula of rhodamine B chlorogallate has been shown to be $(RH)GaCl_4$ where R = rhodamine B.

RÉSUMÉ

Le gallium donne avec la rhodamine B, en présence d'acide chlorhydrique, un composé de formule $(RH)GaCl_4$ (R = rhodamine B).

ZUSAMMENFASSUNG

Es wird nachgewiesen, dass der Gallium–Rhodamin B Komplex die Zusammensetzung $RHGaCl_4$ (R = Rhodamin B) hat.

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VOLUMETRIC DETERMINATION OF PERSULPHATE IN SULPHURIC ACID SOLUTIONS BY PERMANGANATE

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As early as in 1897 it was reported by ELBS[1] that perdisulphuric-acid gradually hydrolyses first to permonosulphuric acid and then to hydrogen peroxide. ELBS AND SCHÖNHERR[2] and later MUGDAN[3], and VON BAYER AND VILLIGER[4] showed that there is a progressive hydrolysis with the increasing concentration of sulphuric acid with the ultimate formation of hydrogen peroxide. PALME[5] advanced the following mechanism for the hydrolysis.

$$H_2S_2O_8 + H_2O \rightleftharpoons H_2SO_5 + H_2SO_4 \quad (1)$$

$$H_2SO_5 + H_2O \rightleftharpoons H_2O_2 + H_2SO_4 \quad (2)$$

The author[6] has confirmed the previous findings and has made some additional observations. It has been found that the amount of hydrogen peroxide produced by the hydrolysis of potassium persulphate reaches a maximum at a particular concentration of sulphuric acid and decreases at higher concentrations of the acid. The amount of hydrogen peroxide produced is equivalent to persulphate in about 12.5 *N* sulphuric acid solution — an observation which led to the present investigation of the quantitative determination of persulphate. To a known volume of persulphate is added the requisite amount of concentrated sulphuric acid and aliquots are titrated with a standard solution of permanganate.

EXPERIMENTAL PROCEDURE

The potassium persulphate and potassium permanganate used were of Merck *p.a.* and B.D.H. quality respectively. Sulphuric acid was of A.R. quality (sp.gr. 1.84) from Orient Scientific Industries, Agra, India. A 5-ml microburette was used and a 5-ml pipette was standardised by the microburette. Persulphate solutions were always freshly prepared by direct weighing and the concentrations were checked by standard methods[7,8].

Preliminary experiments showed that it is best to prepare 50-ml solutions of persulphate in a conical flask for volumetric determination. There are deviations if the total volume is more or less, even though the overall concentration of sulphuric acid is the same. 33.5 ml of the persulphate solution were measured into a 150-ml conical flask and to this were gradually added (0.5 ml at a time) with shaking 16.5 ml of

concentrated sulphuric acid (sp.gr. 1.84) from a burette. The mixture was allowed to cool and 5- or 10-ml aliquots were pipetted and titrated with a standard solution of permanganate from a 5-ml microburette. The end-point was marked by the appearance of pink colour which persisted at least for 10 sec. A blank was also run with a solution of sulphuric acid of the same concentration. The readings were usually concurrent and the average of a number of observations was taken.

5-, 10- or 20-ml portions of persulphate solution may also be taken and the requisite volume of distilled water added to make the volume 33.5 ml before adding 16.5 ml of concentrated sulphuric acid. Table I gives a set of typical results.

TABLE I

Conc. of $KMnO_4$ = 0.01968 N, conc. of $K_2S_2O_8$ = 0.02 N; blank reading = 0.02 ml of $KMnO_4$

Mixture ml	$KMnO_4$ ml	*Average $KMnO_4$ taken for calculation after deducting the blank* ml	*Concentration of $K_2S_2O_8$ found* N	*Error* %
5	5.09			
5	5.10			
5	5.11	5.08	$\frac{0.01968 \cdot 5.08}{5} = 0.01999$	−0.005
5	5.10			
5	5.10			

Some of the observations using different concentrations of the persulphate and the permanganate are shown in Table II.

TABLE II

Blanks for 0.03921 N and 0.009852 N $KMnO_4$ were 0.01 and 0.04 ml respectively

Concentration of $K_2S_2O_8$ taken N	*Reaction mixture titrated* ml	*Concentration of $KMnO_4$* N	*$KMnO_4$ reqd.* ml	*Concentration of $K_2S_2O_8$ found* N	*Error* %
0.04	5	0.03921	5.025	0.03941	−1.49
0.04	5	0.01945	10.12	0.03937	−1.56
0.02	10	0.03921	5.11	0.02003	+0.15
0.02	5	0.01945	5.14	0.01999	−0.005
0.02	5	0.009852	10.14	0.01998	−0.10
0.02	5	0.01968	5.08	0.01999	−0.005
0.01	10	0.01945	5.13	0.009978	−0.22
0.005	10	0.01945	2.565	0.004989	−0.22
0.005	10	0.009852	5.07	0.004995	−0.10
0.004	10	0.01945	2.06	0.004006	+0.15
0.002	10	0.01945	1.03	0.002003	+0.15
0.002	10	0.009852	2.025	0.001995	−0.25
0.001	20	0.01945	1.03	0.001002	+0.20

DISCUSSION

The percentage error in most cases is ± 0.2 or less and hence the method can be recommended for a quick and direct determination of the persulphate. As has been said before peroxide is obtained by the progressive hydrolysis of persulphate according to

the reactions (1) and (2). At higher concentrations of the acid, however, the amount of hydrogen peroxide produced decreases probably because of its decomposition. Table III gives the deviations from the correct result at acid concentrations in the neighbourhood of the recommended one.

TABLE III

Conc. of $KMnO_4$ = 0.01968 *N*, overall conc. of $K_2S_2O_8$ = 0.02 *N*, total volume of reaction mixture = 50 ml, reaction mixture titrated = 5 ml

H_2SO_4 *ml*	*$KMnO_4$* *ml*	*Error* *%*
18.5	5.015	—1.30
18.0	5.03	—1.00
17.5	5.055	—0.50
17.0	5.08	—0.005
16.5	5.08	—0.005
16.0	5.08	—0.005
15.8	5.07	—0.20
15.7	5.03	—0.60
15.5	5.00	—1.60

This table shows that the best acid concentration for the formation of hydrogen peroxide from persulphate is provided by 16.5 ml of concentrated sulphuric acid in 50 ml of solution. At lower concentrations of the acid, the amount of peroxide is less but increases with time, while at higher concentrations, the amount decreases with time. Within the acid concentration range 16–17 ml of concentrated sulphuric acid, there is no change in the amount of hydrogen peroxide even after 72 h. Further it was found that the method is suitable only when the total volume of the reaction mixture is 50 ml. Table IV shows the percentage error for solutions of different volumes, though identical in overall acid concentration.

TABLE IV

Conc. of $KMnO_4$ = 0.01968 *N*, overall conc. of $K_2S_2O_8$ = 0.02 *N*, volume of reaction mixture titrated = 5 ml

Total volume of reaction mixture *ml*	*H_2SO_4* *ml*	*$KMnO_4$ required for 5 ml of reaction mixture* *ml*	*Error* *%*
20	6.6	4.59	—9.60
30	9.9	5.04	—0.80
40	13.2	5.07	—0.20
50	16.5	5.08	—0.005
60	19.8	5.06	—0.40
100	33.0	4.96	—2.40

Heating or diluting the reaction mixtures does not alter the amount of hydrogen peroxide. It is also interesting to note that the method fails if persulphate is added to the acid solution. Only approximately a quarter of the hydrogen peroxide is formed if the addition of the reactants is reversed. In this case the maximum amount of

peroxide is formed at a higher acid concentration (22.5 ml of concentrated sulphuric acid in 50 ml solution), but this corresponds to only 95% of the persulphate.

There is a 5% contraction in the total volume as a result of mixing sulphuric acid with the persulphate solution and there is a 5% decomposition of persulphate or hydrogen peroxide or only 95% persulphate is converted into hydrogen peroxide. However, it is only by chance that the contraction is equal to the decomposition. Hence the method is suitable only under following limitations.

(*1*) The total volume of the reaction mixture should be 50 ml.

(*2*) Sulphuric acid should be added last.

(*3*) 5-, 10- or 20-ml samples should be titrated against the permanganate and not the whole of the reaction mixture.

It may also be mentioned that the persulphate can be determined in a similar manner iodometrically in 10.8 *N* H_2SO_4 when the whole of the persulphate is present in the form of Caro's acid.

SUMMARY

The determination of persulphate in a *ca.* 12.5 *N* sulphuric acid solution by direct titration with permanganate is described. The results are satisfactory but the conditions are critical.

RÉSUMÉ

Une méthode est proposée pour le dosage volumétrique des persulfates, par titrage direct au moyen de permanganate, en présence d'acide sulfurique.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Persulfaten durch direkte Titration mit Permanganat in Gegenwart von Schwefelsäure.

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IODIMETRIC DETERMINATION OF CARBON DISULPHIDE
STUDY OF THE EFFECT OF pH

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Iodimetric determination of carbon disulphide was first proposed by DELACHANAL AND MERMET[1]; alkali xanthate is formed and the mixture is acidified with acetic acid and titrated directly with standard iodine solution in presence of starch. The reaction is:

$$2\ C_2H_5{-}O{-}\overset{\overset{S}{\|}}{C}{-}S{-}K + I_2 \rightarrow (C_2H_5{-}O{-}\overset{\overset{S}{\|}}{C}{-}S)_2 + 2\ KI$$

GASTINE[2] suggested that the titration should be carried out in neutral or slightly alkaline solution and recommended the addition of excess sodium bicarbonate after acidification with acetic acid. RUPP AND KRAUSS[3] also recommended the use of bicarbonate, although their data showed that more iodine was then consumed than in acidified medium. HALBAN AND KIRSCH[4] showed that the reaction was not affected by excess of bicarbonate, but was greatly influenced by most organic solvents. The method was reported as inaccurate by ANDRÉ[5].

More recently, MATUSZAK[6] studied the reaction and confirmed that high results are obtained in presence of excess of bicarbonate (owing to the rapid disappearance of the blue end-point). Avoidance of excess bicarbonate, cooling of the solution in an ice bath, and the use of fresh alcoholic potash solution for the preparation of xanthate gave satisfactory results.

It is obvious that the reaction must depend greatly on the pH of the titrated solution, and that, to obtain quantitative results, it must be carried out under precisely defined conditions. In acid medium, there will clearly be a tendency for the xanthate to decompose and the extent of decomposition is influenced by the hydrogen ion concentration. On the other hand, if the solutions are neutralized (after acidification) with sodium bicarbonate, high results are obtained, presumably owing to the consumption of some iodine by the dixanthogen formed as a result of the primary (forward) reaction. No quantitative data on the kinetics of this reaction have been published, but it appears that the reaction would be accelerated with increase of pH.

The present study was intended to clarify the effect of acidity on the decomposition of xanthate and also whether this decomposition can be retarded sufficiently by using acetate as a buffering agent in place of excess bicarbonate. It is shown that if the titration is carried out within a narrow pH-range in acetic acid–acetate buffered

solutions, satisfactory results are obtained and the reaction can be utilized for accurate determinations of carbon disulphide.

EXPERIMENTAL

The accurate weighing of the carbon disulphide presented some difficulties and the following procedure was finally adopted. First a small amount of alcoholic potassium hydroxide was weighed in a weighing bottle. About 0.2 g of carbon disulphide (pure reagent quality) was added and the bottle was reweighed. It was noted that during the time interval, the alcoholic hydroxide itself lost some weight. A large number of experiments showed that if the same amount of alcoholic hydroxide and the same time were taken for weighing, the loss of weight was always the same at room temperature (25–27°). It was thus decided to use 25 ml of 10% alcoholic hydroxide and to carry out the weighing so that the weighing bottle was kept open for *exactly* 30 sec in each experiment. Under such conditions the weight of the carbon disulphide taken had to be corrected by the loss determined by a blank experiment.

The contents of the weighing bottle were washed into 25 ml of 10% alcoholic potassium hydroxide. The excess alkali was neutralized with glacial acetic acid to a phenolphthalein end-point. The solution was then treated with further acid and/or sodium acetate as desired, and diluted to a volume of 250 ml before titration with standard 0.1 *N* iodine solution in presence of starch indicator.

REAGENTS

Fresh alcoholic potassium hydroxide (10%)

This solution was prepared by dissolving 10 g of A.R. potassium hydroxide in 100 ml of absolute alcohol and then cooling the solution in running water.

Iodine solution (0.1 N)

This solution was prepared by dissolving 12.7 g of resublimed A.R. iodine in 100 ml of distilled water containing 40 g of A.R. potassium iodide and then diluting to one litre with distilled water. The solution was standardised against 0.1 *N* $Na_2S_2O_3$ which had been standardised against standard $K_2Cr_2O_7$ solution.

EFFECT OF TIME INTERVAL BETWEEN ACIDIFICATION AND TITRATION

It is quite possible that in acid medium some decomposition of the xanthic acid would take place, and thus cause low results for sulphur; the extent of decomposition would depend on the time taken for the titration. The results presented in Table I show that

TABLE I

EFFECT OF TIME INTERVAL BETWEEN ACIDIFICATION AND BEGINNING OF TITRATION

Time interval (min)	*Corrected wt. of CS_2 taken g*	*Sulphur present g*	*Sulphur found g*	*Error %*
1	0.2254	0.1898	0.1890	—0.5
2	0.2154	0.1814	0.1772	—2.3
3	0.2528	0.2129	0.2078	—2.5
5	0.2742	0.2309	0.2209	—4.4
10	0.2160	0.1819	0.1684	—7.5
20	0.2492	0.2098	0.1803	—14.0

the decomposition does occur to an extent which may vitiate the titration altogether.

In these experiments, the excess alkali was first neutralized with glacial acetic acid (1.8 ml) and then 1 ml of acid was added to give pH 5. The time interval between this acidification and the beginning of the titration was varied; the time taken for the actual titration was kept constant (45 sec). The Table shows that significant results were only obtained when the titration was started within a minute of acidification; otherwise the decomposition was appreciable. It will be seen later that the rate of decomposition is much slower at higher pH.

EFFECT OF pH

Another set of experiments was carried out in which the timing was kept constant (2 min plus 45 sec for titration), but the pH was lowered below 5. The results shown in Table II confirm that the extent of decomposition also depends on the acid concentration and for satisfactory titration, the pH must exceed 5. When no excess of acetic acid is added (pH = 7.7), there is a moderate positive error, which indicates that the pH should be between 5.0 and 7.0.

The results shown in Table III were obtained when the pH was adjusted by adding

TABLE II

EFFECT OF pH

Excess acetic acid added ml	*pH*	*(Corrected) wt. of CS_2 taken g*	*Sulphur present g*	*Sulphur found g*	*Error %*
0	7.7	0.2018	0.1699	0.1735	+ 2.0
0	7.7	0.2170	0.1826	0.1861	+ 1.9
1	5.0	0.3038	0.2558	0.2483	— 2.9
2	4.7	0.2594	0.2184	0.2077	— 4.9
3	4.5	0.2138	0.1801	0.1692	— 6.1
5	4.3	0.1874	0.1578	0.1435	— 9.1
10	4.1	0.2492	0.2098	0.1691	—19.4

TABLE III

EFFECT OF USING VARYING AMOUNTS OF SODIUM ACETATE IN CONJUNCTION WITH A SMALL EXCESS OF ACETIC ACID

Excess acetic acid used = 1.0 ml for expts. 1 to 6 and 0.5 ml for expts. 7 to 12

Expt. No.	*Sodium acetate used g*	*pH*	*Correct wt. of CS_2 taken g*	*Sulphur present g*	*Sulphur found g*	*Error %*
1	0	5.0	0.2154	0.1814	0.1772	—2.3
2	2	5.2	0.1828	0.1539	0.1522	—1.1
3	5	5.4	0.2334	0.1965	0.1960	—0.3
4	10	5.6	0.2246	0.1892	0.1890	—0.10
5	15	5.7	0.2152	0.1811	0.1810	—nil
6	20	5.8	0.2238	0.1883	0.1884	+nil
7	0	5.3	0.2456	0.2068	0.2059	—0.4
8	2	5.6	0.2544	0.2142	0.2140	—0.1
9	5	5.8	0.1952	0.1644	0.1653	+0.5
10	10	6.0	0.2656	0.2236	0.2259	+1.0
11	15	6.1	0.2140	0.1802	0.1816	+0.8
12	20	6.25	0.2140	0.1802	0.1832	+1.6

a slight excess of acetic acid (1.0 or 0.5 ml of glacial acetic acid) followed by varying amounts of sodium acetate. It can be seen (see also Fig. 1) that there is no decomposition of xanthate in the pH range 5.7 and 5.8; but a wider pH range from 5.4 to 6.0 can be employed if an error of $\pm 1.0\%$ can be tolerated. Optimally, the titrating

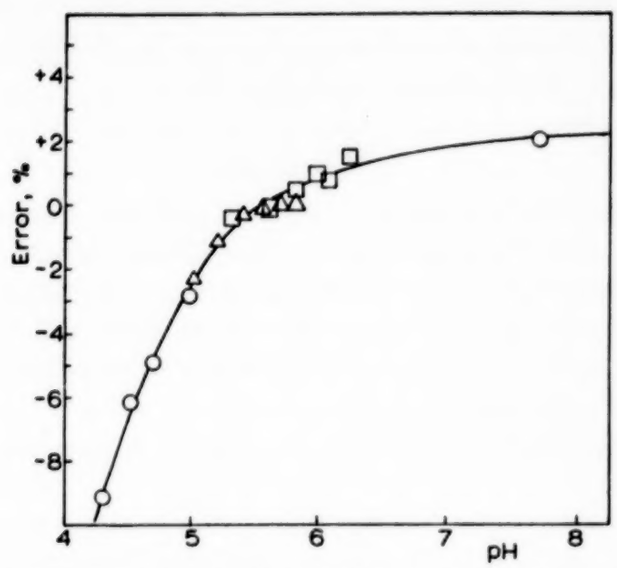

Fig. 1. Effect of pH on iodimetric determination of CS_2. –O– data from Table II; –△– data from Table III (top); –□– data from Table III (bottom).

solution should be first neutralized (to the phenolphthalein end-point) with acetic acid and then 0.5 ml of acetic acid added together with 2–5 g of sodium acetate before the titration. If more of acetic acid (1.0 ml) is added, more sodium acetate (5–15 g) is required. Under these conditions, carbon disulphide can be satisfactorily determined.

It has been seen that at a pH of 5.0 or below, a time interval of even one or two minutes between the acidification and the beginning of the titration was unsatisfactory. However, higher pH values in the range of 5.4–5.8 gave satisfactory results for a time interval of two minutes. The data in Table IV show that at pH 5.4 the rate of decomposition is considerably slower and a time interval of even ten minutes can be safely allowed. In these experiments 1 ml of acetic acid and 5 g of sodium acetate were added.

TABLE IV

EFFECT OF TIME INTERVAL BETWEEN ACIDIFICATION AND BEGINNING OF TITRATION AT PH 5.4

Time interval (min)	*Corrected wt. of CS_2 taken g*	*Sulphur present g*	*Sulphur found g*	*Error %*
1	0.2208	0.1861	0.1869	+0.5
2	0.2082	0.1753	0.1760	+0.4
3	0.2144	0.1806	0.1805	nil
5	0.2252	0.1895	0.1882	—0.7
10	0.1840	0.1549	0.1536	—0.9
20	0.2170	0.1827	0.1760	—3.7

RESULTS WITH VARYING QUANTITIES OF CARBON DISULPHIDE

With the optimum conditions indicated above (*i.e.* at pH 5.4) it was shown that amounts of carbon disulphide varying between 0.0060 g and 0.3240 g could be satisfactorily determined by this method (Table V). It should, however, be pointed out that for very small quantities of disulphide, the titrations should be carried out with great care and with a micro-burette.

TABLE V

EFFECT OF VARIATION OF THE AMOUNT OF CS_2

Expt. No.	*Acetic acid needed for neutralization* ml	*Corrected wt. of CS_2 taken* g	*Sulphur present* g	*Sulphur found* g	*Error* %
1	1.9	0.0061	0.0051	0.0051	nil
2	1.9	0.0122	0.0102	0.0102	nil
3	1.9	0.0183	0.0154	0.0154	nil
4	1.9	0.0277	0.0233	0.0233	nil
5	1.9	0.0554	0.0467	0.0472	+1.0
6	1.9	0.1022	0.0860	0.0861	+0.1
7	1.9	0.1227	0.1033	0.1040	+0.7
8	1.9	0.1442	0.1214	0.1222	+0.7
9	1.8	0.1874	0.1578	0.1581	+0.2
10	1.8	0.2082	0.1753	0.1760	+0.4
11	1.8	0.2474	0.2083	0.2070	−0.6
12	1.8	0.2650	0.2231	0.2214	−0.8
13	1.7	0.3240	0.2728	0.2720	−0.3

SUMMARY

The effects of pH and time on the error (due to decomposition of xanthate) involved in the iodimetric determination of carbon disulphide have been studied. A pH range of 5.4 to 5.8 (acetate-buffered) is recommended. Carbon disulphide varying in amount from 0.0060 to 0.3240 g can be determined with an error of ±1.0%.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'influence du pH lors du dosage iodimétrique du sulfure de carbone.

ZUSAMMENFASSUNG

Untersuchung über den Einfluss des pH auf die jodometrische Bestimmung des Schwefelkohlenstoffs.

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DOSAGE COMPLEXOMÉTRIQUE DE CHLORURES, CHLORATES ET PERCHLORATES EN PRÉSENCE LES UNS DES AUTRES

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Nous avons décrit une méthode pour la détermination simultanée de chlorates et perchlorates en présence l'un de l'autre[1]. À présent nous présentons la technique pour le dosage complexométrique des chlorures, chlorates et perchlorates dans un mélange. La méthode décrite a l'avantage de pouvoir doser les trois ions en moins de 4 heures, alors que les procédés classiques prennent de 5 à 6 heures. En outre, la précision est très satisfaisante.

FLASCHKA[2] et HUDITZ[3] ont utilisé le complexon-III pour la détermination de chlorures, en dissolvant le précipité de chlorure d'argent dans une solution ammoniacale de nickel–tétracyanure. Les réactions se passent comme suit:

$$2\ AgCl + [Ni(CN)_4]^{-2} \rightarrow 2[Ag(CN)_2]^- + Ni^{+2} + 2\ Cl^-$$

Le nickel déplacé est dosé par voie complexométrique et l'halogène est ainsi déterminé indirectement.

Lorsqu'on ajoute du nitrate d'argent à un mélange de chlorures, chlorates et perchlorates, seuls les chlorures sont précipités. De cette façon, nous pouvons déterminer les chlorures.

Les chlorates doivent être réduits en chlorures pour pouvoir être déterminés par la méthode ci-dessus. Une réduction appropriée est utilisée pour réduire seulement les chlorates, laissant les perchlorates dans leur état initial.

Au moyen d'une réduction plus intense, les chlorates et les perchlorates sont transformés en chlorures et les trois composés du chlore sont précipités en chlorure d'argent.

Les chlorates contenus dans le mélange peuvent être réduits en chlorures en additionnant du sulfate ferreux ou du zinc en poudre à la solution acidifiée (acide acétique). Ces deux procédés de réduction n'affectent pas les perchlorates.

La réduction des perchlorates est effectuée au moyen d'un chauffage du mélange (à l'état solide) avec environ 5 fois le poids de chlorure d'ammonium. Au cours de cette opération, les chlorates sont aussi réduits en chlorures. Le mélange, résultant après réduction ne contient pourtant que des chlorures qui peuvent être précipités par le nitrate d'argent.

Ayant trois précipités de chlorure d'argent, correspondant (1) aux chlorures, (2) aux chlorures et aux chlorates, (3) aux chlorures, chlorates et perchlorates contenus dans le mélange, il est possible de déterminer chacun des composés par voie complexométrique.

Reactifs

Chlorure d'ammonium *(pro analisi)*; solution de sulfate ferreux cristallisé à 10%; solutions de nitrate d'argent à 5% et 0.1%; solution d'acide nitrique à 1%; solution de complexon-III 0.1 *M*; solution saturée de murexide (aqueuse); solution ammoniacale de nickel-tétracyanure 0.1 *M*, obtenue par titrage précis d'une solution de sulfate de nickel 0.1 *M* par une solution de cyanure de potassium 1 *M* après addition d'ammoniaque, le titrage est terminé lorsque l'indicateur (murexide) vire du jaune au violet.

MODE OPÉRATOIRE

Une portion de l'échantillon à l'état de poudre est traitée avec cinq fois son poids de chlorure d'ammonium dans une capsule de platine. On mélange le tout intimement. On recouvre le mélange avec une couche de chlorure d'ammonium et l'on chauffe doucement pendant 1 à 2 h après avoir couvert la capsule avec un verre de montre.

Au cas où l'on utilise une capsule de porcelaine, il faut ajouter au mélange 1 ml d'acide chloroplatinique. On doit veiller à ce que la température du mélange soit au-dessous du point de fusion du chlorure résiduel (sinon on risque d'attaquer les parois de la capsule de platine). On ajoute encore du chlorure d'ammonium et l'on chauffe doucement pendant une demi-heure. On laisse refroidir et l'on dissout les chlorures dans l'eau distillée contenue dans un bécher. On ajoute de l'acide nitrique, puis l'on précipite tous les chlorures à l'aide de nitrate d'argent à 5%. On porte le contenu du bécher à l'ébullition pendant 5 min en prenant soin de couvrir le bécher avec un verre de montre.

On refroidit la solution et l'on filtre sur un Gooch. Le précipité est lavé avec une solution de nitrate d'argent à 0.1%. Il (A) est mis de côte pour être dissous dans la solution de tétracyanure de nickel.

Dans une seconde portion de l'échantillon, les chlorates sont réduits au moyen de sulfate ferreux. La prise d'échantillon est dissoute dans l'eau distillée, puis traitée par 50 ml d'une solution de sulfate de fer(II) à 10%. On chauffe à l'ébullition tout en agitant pendant 15 min. On ajoute l'acide nitrique jusqu'à ce que le sel ferrique basique soit complètement dissous. Les chlorures sont précipités ensuite par le nitrate d'argent. Le précipité (B) est lavé comme dans le cas de (A) puis mis de côté pour le titrage complexométrique.

Une troisième portion de l'échantillon est dissoute dans 100 ml d'eau distillée. On ajoute quelques gouttes d'acide nitrique à la solution jusqu'à réaction acide. Les chlorures sont précipités ensuite par addition de nitrate d'argent. Le précipité (C) est lavé et filtré comme indiqué ci-dessus, puis introduit avec le filtre Gooch dans un bécher de 500 ml contenant la solution ammoniacale de nickel-tétracyanure. On chauffe doucement en agitant jusqu'à dissolution complète du précipité. On ajoute quelques gouttes d'indicateur (murexide) et l'on titre le nickel libéré avec la solution de complexon-III, jusqu'à ce que la couleur de la solution vire au violet. Pour connaître la quantité de Cl^- en mg, il faut multiplier le nombre de ml de complexon-III par 7.0914.

Les précipités (A) et (B) sont traités d'une façon identique et la quantité totale de chlorures est déterminée dans chaque cas. La différence en ml entre les titrages des précipités (B) et (C) donne la quantité de ClO_3^- en mg en multipliant par 16.691.

La différence en ml des titrages des précipités (A) — [(B) + (C)] multipliée par

19.891 donne la quantité en mg de ClO_4^- contenue dans le mélange. Ainsi, on obtient le dosage des trois composés de chlore. Les résultats sont très satisfaisants et la méthode a l'avantage d'être plus rapide que celle de la gravimétrie.

RÉSUMÉ

Une méthode est décrite pour le dosage d'un mélange de chlorures, chlorates et perchlorates par voie complexométrique. Les chlorates et les perchlorates sont réduits à l'état de chlorures au moyen de réducteurs appropriés et précipités ensuite sous forme de chlorure d'argent. Ces précipités (respectifs aux chlorures, chlorates et perchlorates) sont dissous dans une solution ammoniacale de nickeltétracyanure et l'ion Ni^{+2} déplacé par la réaction est titré au moyen du complexon-III. Le chlorure est déterminé indirectement. Trois titrages sont nécessaires pour obtenir les valeurs en mg de Cl^-, ClO^- et de ClO_4^-. Le premier titrage donne la somme des chlorures (après réduction des chlorates et perchlorates). Un second titrage donne la quantité de chlorures après réduction des chlorates seulement et le troisième fournit les chlorures existant dans le mélange. Au moyen de facteurs appliqués aux lectures de burette, on obtient la teneur des trois composés du chlore. La méthode est rapide et sensible. Des essais faits avec des mélanges artificiels ont donné des résultats satisfaisants.

SUMMARY

A method is described for the analysis of a mixture of chlorides, chlorates and perchlorates by complexometric titration. It is based on the partial reduction of chlorates and the reduction of chlorates plus perchlorates respectively; the chloride formed can then be determined.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Analyse eines Gemisches von Chloriden, Chloraten und Perchloraten durch komplexometrische Titration. Das Verfahren beruht auf der partiellen Reduktion des Chlorates bezw. der Reduktion des Chlorates + Perchlorates und Bestimmung des gebildeten Chlorids.

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THERMOGRAVIMETRIC CHARACTERISTICS OF BARBITURIC ACID AND SOME OF ITS DERIVATIVES

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INTRODUCTION

5-Nitrobarbituric acid has been used for the determination of metal cations[1-5] and organic bases[5,6]. The thermogravimetric characteristics of some inorganic and organic salts of 5-nitrobarbituric acid have been given by the authors in previous papers[4,6]. The thermogravimetric characteristics of barbituric acid, dilituric acid (5-nitrobarbituric acid), violuric acid (5-isonitrosobarbituric acid), 1,3-dimethylvioluric acid and barbital (5,5-diethylbarbituric acid) are presented in this paper.

HOTCHKISS AND JOHNSON[7] reported that dibarbituric acid is formed by the loss of one mole of water of composition per two moles of barbituric acid when the latter is heated in glycerol at 170°. The authors have been interested in observing if such a reaction also took place in the solid state.

Dilituric acid, as stated previously, has been used for gravimetric determinations. Thermal stability studies of dilituric acid and the dilituric should prove of value in investigating the proper temperature of heating the dilituric. Such a temperature should be high enough to decompose or sublime any coprecipitated dilituric acid but not high enough to decompose the dilituric.

Violuric and 1,3-dimethylvioluric acid have been used by TAYLOR[8] for the spectrophotometric determination of the alkali and alkaline earth metals. A thermogravimetric study of these acids and salts is reported in this paper to indicate the degrees of hydration as well as the range of stabilities of the anhydrous compounds.

The decomposition of barbital has also been made to study the effect of alkyl substituents in the 5 position on the decomposition.

EXPERIMENTAL

Preparation and purification of the acids

Barbituric acid. Technical grade barbituric acid from Eastman Organic Chemicals was recrystallized from 50% ethanol solution, washed with ether and dried in air overnight.

Dilituric acid. Technical grade dilituric acid from Eastman Organic Chemicals was recrystallized from water and dried in air overnight.

Violuric acid. Technical grade violuric acid from Eastman Organic Chemicals was recrystallized from a 50% ethanol solution and dried in air overnight.

1,3-Dimethylvioluric acid. The method used for the preparation of 1,3-dimethyl-

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violuric acid was essentially that of BILTZ[9] and BILTZ AND HAMBURGER[10] with minor modifications.

Barbital. Barbital, from Eastman Organic Chemicals was used directly without further recrystallization.

Apparatus

An A.D.A.M.E.L. recording thermobalance (Chevenard System) was used to obtain the thermolysis curves. The samples were heated in No. 000 porcelain crucibles, having a volume of about 6 ml.

PROCEDURE

The samples were in the form of powders passing through a 65-mesh sieve. All the compounds were heated in air with the exception of violuric acid, which was run in dry nitrogen, flowing at the rate of 2 l/h. The weights of the samples and the corresponding rates of heating are given in the figures.

In the graphical representations of the thermogravimetric decompositions we have normalized the curves to a percentage change in weight *vs.* temperature. In this way differences in weight of the samples are eliminated and comparison is easier.

Another way of presenting these thermogravimetric decompositions is by a plot of the change in the apparent molecular weight *vs.* temperature. Such plots give a direct measurement of the molecular weight of the fraction decomposing and permit an easy correlation between reactions of similar compounds. An example of such a representation will be shown.

RESULTS AND DISCUSSION

The thermal decomposition curves of barbituric, dilituric and violuric acids are shown in Fig. 1, with the data normalized for percentage decomposition. The thermal decomposition curves of 1,3-dimethylviolurie acid and of barbital are shown in Fig. 2. In Fig. 3 we have the decomposition curves of the same acids as in Fig. 1 but the data in this case have been normalized with respect to changes in the apparent molecular weight. A differential thermal analysis curve for the dehydration and decomposition of dilituric acid is shown in Fig. 4.

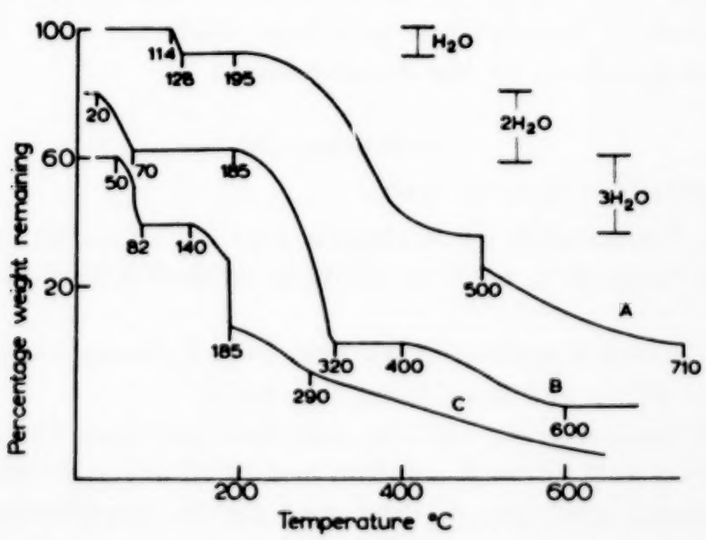

Fig. 1. Thermal decomposition of derivatives of barbituric acid. A. Violuric acid, 45.3 mg heated at 65°/h; B. Barbituric acid, 88.9 mg heated at 65°/h; C. Dilituric acid, 69.3 mg heated at 65°/h.

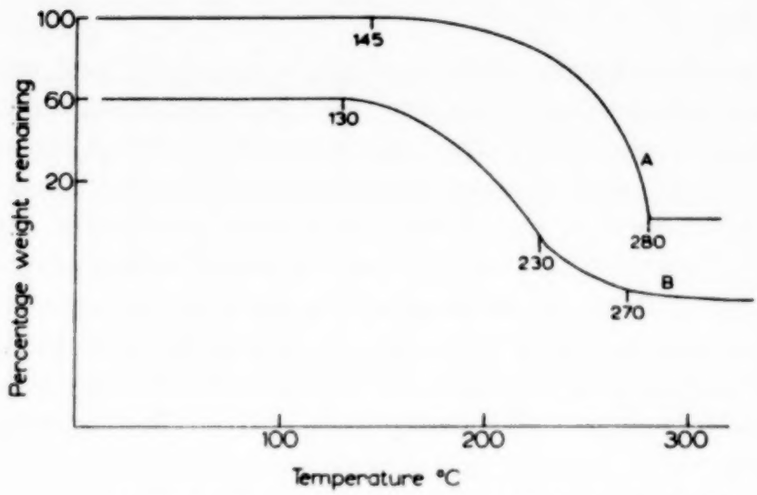

Fig. 2. Thermal decomposition of derivatives of barbituric acid. A. Barbital, 31.8 mg heated at 65°/h; B. 1,3-Dimethylvioluric acid, 40.0 mg heated at 65°/h.

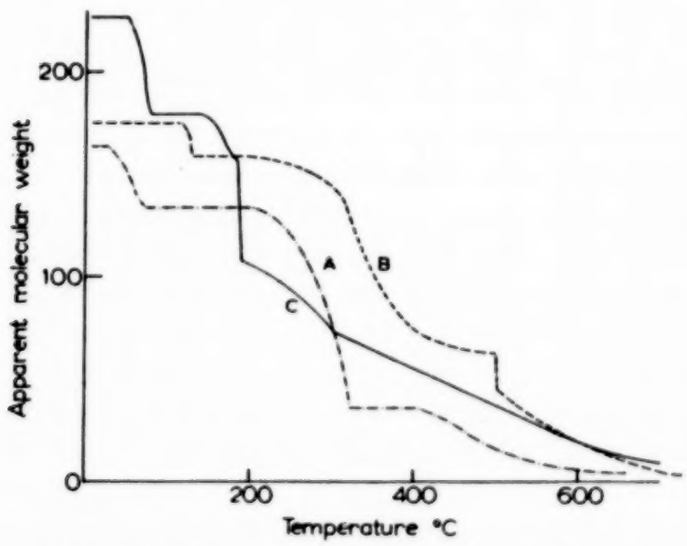

Fig. 3. Thermal decomposition of derivatives of barbituric acid. Curves normalized with respect to changes in the apparent molecular weight. A. Barbituric acid, 88.9 mg heated at 65°/h; B. Violuric acid, 45.3 mg heated at 65°/h; C. Dilituric acid, 69.3 mg heated at 65°/h.

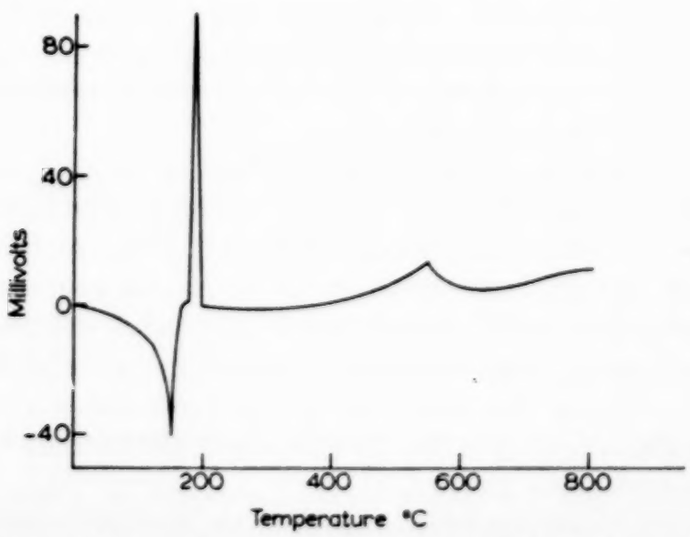

Fig. 4. Differential thermal decomposition of dilituric acid, heated at 300°/h.

Barbituric acid (Fig. 1)

The dehydration of barbituric acid dihydrate began at 20° and terminated at 70°. In spite of the easy dehydration, this water must be water of crystallization since the precipitate had been washed with ether, and normally water of absorption would be removed by this treatment. Anhydrous barbituric acid was stable to 180°. An accelerated loss in weight followed to 320°. From 320° to 400° the residue, representing 22% of the initial weight, was stable. If dibarbituric acid had been formed by a solid state reaction a plateau or a break in the slope of the thermolysis curve would have been observed corresponding to a loss in weight of 27.5%. No such break occurred; we can therefore conclude that dibarbituric acid is not formed by thermal decomposition. The stable residue formed at 320° decomposed slowly to 600° at which temperature no residue was left.

Dilituric acid (Fig. 2)

A trihydrate was formed upon recrystallization from water which dehydrated between 50° and 90°. A more complete discussion of the dehydration of dilituric acid and of the kinetics of this dehydration will be given in a later paper. The anhydrous form of dilituric acid was stable to 140°. A decomposition then was initiated and at 185° dilituric acid exploded, even though there was a low rate of heating. It appears that this explosion will occur under any heating conditions since an explosion also occurred after a certain time, when dilituric acid was heated at a constant temperature of 150°. This is reasonable in view of the high exothermicity of the autocatalytic reaction as shown by the differential thermal curve in Fig. 4. The residue, left after the explosion, decomposed very slowly to 700° where no residue remained.

Dilituric acid is an almost white crystalline compound which dissolves in water to yield a yellow solution with high absorbancy at 380 mμ. The ultraviolet spectrum of this solution was more complex having peaks at 218 and 318 mμ and a shoulder at 237 mμ. It seems that the 218-mμ peak is due to the primary ionization of dilituric acid, while the 318-mμ peak is due to a secondary ionization and is strongly dependent upon the pH of the solution.

The thermal decomposition product of dilituric acid which appeared just before the explosion had a deep red color; it was more easily soluble in water than dilituric acid itself giving a deep red solution with high absorbancy at 520 mμ. This absorption peak disappeared completely within 3 h. The pH of such a solution was about 3 and did not change with the change in color.

If this same decomposition product was dissolved in ethanol then the absorption peak was shifted to 450 mμ and it had a higher stability. The U.V. absorption spectrum of the residue of dilituric acid was only slightly different from that of dilituric acid itself, the peaks having been shifted to 212, 311 and 249 mμ respectively.

Let us note finally that upon evaporation of the faded solution the original red residue was obtained again. This substance dissolved in water forming a red solution which faded on standing in the same manner as the original red solution. This is an indication that the red color is due to an anhydrous form and that the decay is simply a reversible hydrolytic process.

The infrared spectrum of the residue showed the complete disappearance of the 6.75-, 6.95- and 7.00-μ peaks of dilituric acid due to the nitro group.

Violuric acid (Fig. 1)

The monohydrate of violuric acid was quite stable. Dehydration took place between 114° and 130°. The anhydrous form was stable up to 195°. A S-shaped decomposition curve followed to 500° where an explosive like break occurred in the thermolysis curve. The decomposition was terminated at 715°.

1,3-Dimethylvioluric acid (Fig. 2)

This acid did not form a hydrate. Sublimation started at 130° and proceeded without side reactions to 230°, where 28% of the initial weight remained. With the inflection point at 230° the differential change in weight became less accentuated. This can be interpreted as due to coating of the undecomposed dimethylvioluric acid with decomposition product rendering further sublimation difficult. Another break in the curve occurred at 270° indicating a further reduction in the differential change in weight. The residue disappeared completely at 370°.

The decomposition curve of 1,3-dimethylvioluric acid obtained at a rate of heating of 300°/h had an inflection point at 275°. There was a 50% loss in weight, indicating decomposition as the major process whereas sublimation predominated at the slower rate of heating.

Barbital (Fig. 2)

Barbital was also present as the anhydrous compound. It started to sublime at 145° accelerating to 280° where no residue remained.

Comparing the various thermolysis curves it is seen that substitution of an alkyl group for a hydrogen either on the nitrogen or on the 5 carbon makes the resulting compound less stable and with a greater tendency to sublime. The stability of the unsubstituted compound can be attributed to hydrogen bonding within the crystal lattice.

SUMMARY

The thermolysis curves of barbituric acid and some of its derivatives have been determined. Barbituric acid, violuric acid and dilituric acid form hydrates while 1,3-dimethylvioluric acid and barbital are anhydrous. Barbital and 1,3-dimethylvioluric acid sublime before decomposition. The differential thermal analysis for dilituric acid showed a sharp exotherm at 190° indicating a violent explosion.

RÉSUMÉ

Les auteurs ont examiné les courbes de pyrolyse de l'acide barbiturique et de quelques-uns de ses dérivés: acide violurique, acide dilituriqué, acide diméthyl-1,3-violurique et barbital.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über das thermolytische Verhalten von Barbitursäure und einigen Barbitursäurederivaten.

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THERMOGRAVIMETRIC AND MAGNETIC CHARACTERISTICS OF SOME INORGANIC SALTS OF DILITURIC ACID

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INTRODUCTION

The thermogravimetric characteristics of barbituric acid, its 5-substituted derivatives, the organic salts of 5-nitrobarbituric acid and of the diliturates of potassium, magnesium and lead have been reported previously[1-3].

We have determined the degrees of hydration and the thermal decomposition curves of the diliturate salts which have been used for the gravimetric determination of the respective cations (copper[4], nickel[5], cadmium[6], cobalt(II)[7]). We have established the thermal characteristics of the diliturate salts which could be used for the determination of the corresponding cations (iron(II), zinc).

The magnetic susceptibilities of cobalt and iron diliturates have also been investigated to get a better idea of the nature of the bonds formed between the metal cation and the organic portion of the molecule.

EXPERIMENTAL

Reagents and metal diliturates

Dilituric acid solution. The solution used for the preparation of the metal diliturates was an aqueous solution saturated at 25°.

Ammonium diliturate. An excess of dilituric acid solution was added to a 0.1-*M* aqueous solution of reagent grade ammonium chloride. Ammonium diliturate precipitated immediately; it was filtered, washed with water and dried in air.

Rubidium diliturate. Reagent grade rubidium chloride was used for the preparation of rubidium diliturate. The method of preparation was similar to that for ammonium diliturate.

Iron(II) diliturate. An excess of hot dilituric acid solution was added to a 0.1-*M* aqueous solution of recrystallised $Fe(NH_4SO_4)_2 \cdot 6\ H_2O$. The iron(II) diliturate hexahydrate precipitate was filtered, washed with water and dried in air.

Cobalt(II) diliturate. An excess of dilituric acid solution was added to a 0.1-*M* aqueous solution of reagent grade cobalt(II) nitrate from the Allied Chem. and Dye Co. The cobalt(II) diliturate hexahydrate was treated similarly to iron(II) diliturate.

Nickel diliturate. Reagent grade nickel nitrate was used for the preparation of nickel diliturate hexahydrate. The preparation was similar to that of cobalt(II) diliturate.

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Copper dilituratе. An excess of a saturated solution of dilituric acid in ethanol (50%) was added to a 0.017-*M* solution of copper nitrate which had been prepared by dissolving copper metal in nitric acid. The copper dilituratе octahydrate precipitate which formed was cooled in an ice bath, filtered, washed twice with a 0.02% solution of dilituric acid in alcohol, twice with 95% ethanol and finally with anhydrous ether.

Zinc dilituratе. An excess of saturated dilituric acid solution in 50% ethanol was added to a dilute aqueous solution of reagent grade zinc chloride, Allied Chemicals and Dye Co. The resultant mixture was heated, then cooled slowly and finally in ice. Zinc dilituratе hexahydrate precipitate was filtered, washed with 95% ethanol and dried in vacuo (water pump).

Cadmium dilituratе. An excess of saturated dilituric acid solution was added to a 0.01-*M* aqueous solution of analytical reagent grade cadmium chloride, Mallinckrodt Chemical Works. The resultant mixture was heated, cooled slowly, finally in ice. The cadmium dilituratе octahydrate precipitate was filtered, washed with a 0.02% solution of dilituric acid in alcohol and then dried with acetone. The precipitate was further dried in a vacuum desiccator.

Carbon and hydrogen analyses of the above compounds are as follows (see Table I):

TABLE I

Salt	*Calculated*		*Analysed*	
	%*C*	%*H*	%*C*	%*H*
Rubidium dilituratе				
$RbC_4N_2H_2O_3 \cdot NO_2$	18.65	0.78	18.58	0.99
Mol. wt. 257.6			18.39	0.74
Zinc dilituratе hexahydrate				
$Zn(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 6\ H_2O$	18.56	3.12	17.61	3.56
Mol. wt. 517.7			17.50	3.51
Cadmium dilituratе octahydrate				
$Cd(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 8\ H_2O$	15.99	3.36	15.26	3.37
Mol. wt. 600.8			15.46	3.14
Cobalt dilituratе hexahydrate				
$Co(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 6\ H_2O$	18.79	3.16	18.52	3.52
Mol. wt. 511.3			18.27	3.42
Iron dilituratе hexahydrate				
$Fe(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 6\ H_2O$	18.91	3.18	18.29	3.68
Mol. wt. 508.2			17.95	3.63
Nickel dilituratе hexahydrate				
$Ni(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 6\ H_2O$	18.80	3.16	18.32	3.40
Mol. wt. 511.0			18.02	3.53

Apparatus

An ADAMEL recording thermobalance (Chevenard System) was used to obtain the thermolysis curves. A magnetic susceptibility balance similar to the one described by IHRIG AND CALDWELL[8] was assembled. Due to the low sensitivity of the balance and to the weak magnetic field strength (3700 ± 200 gauss) it was not necessary to enclose the system in a glass container.

Procedure

The samples for the thermolysis determinations were in the form of powders passing through a 65-mesh sieve. They were placed in No. 000 porcelain crucibles, having a volume of about 6 ml. All the compounds were run in air excepting cadmium dilituratе which was run in dry nitrogen flowing at the rate of 2 l/h. The weights of the samples and the rates of heating are given in the Figs. In the graphical representation of the thermogravimetric decompositions we have normalized the curves to a percentage change in weight *vs.* temperature.

The method described by SELWOOD[9] was used for calculating the molar paramagnetism χ_M and the permanent effective moment μ_{eff} from the changes in weight of the sample produced by the application of the magnetic field. The magnetic susceptibility balance was calibrated with hydrated ferrous ammonium sulfate. The number of unpaired electrons was related to the permanent effective moment using the expression given by PAULING[10]

$$\mu_{eff} = \sqrt{n(n+2)}$$

RESULTS AND DISCUSSION

Thermolysis curves

The thermal decomposition curves of ammonium and rubidium dilituratеs are given in Fig. 1. Alkali metals and ammonium form stable anhydrous salts with dilituric acid.

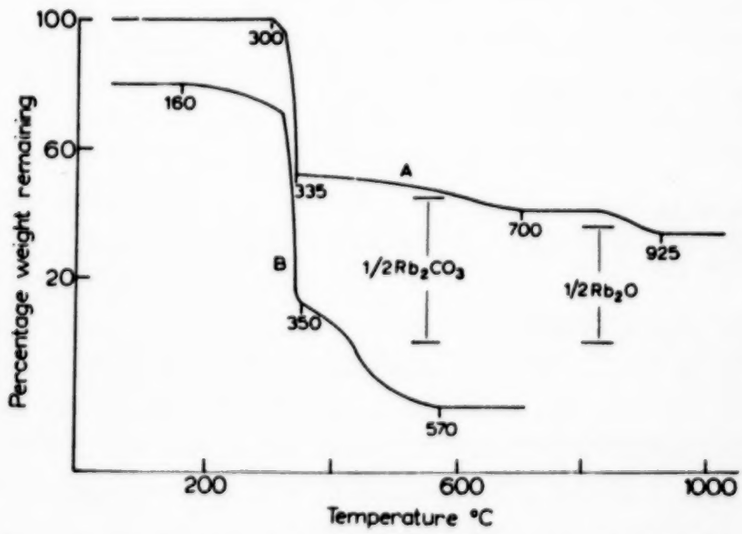

Fig. 1. Thermal decomposition curves. A, Rubidium dilituratе, 90.7 mg heated at 300°/h; B, Ammonium dilituratе, 131.2 mg heated at 300°/h.

Ammonium dilituratе. Anhydrous ammonium dilituratе was stable to 160°. A fast decomposition took place up to 350° followed by a decomposition with a S-shaped curve terminating at 570° where no residue remained.

Rubidium dilituratе. The decomposition of rubidium dilituratе was similar to that of potassium dilituratе[3] with the exception that the anhydrous form was stable to 300° and that RbO was formed at 925°.

The thermal decomposition curves of iron(II), cobalt(II), and copper dilituratеs are

given in Fig. 2, while those for nickel, zinc and cadmium dilituratés are given in Fig. 3.

Iron(II) dilituratе. Iron(II) dilituratе formed an hexahydrate stable to 80°. A one-step dehydration followed terminating at 200°. The anhydrous compound which resulted was stable to 230°. An explosive decomposition followed to 270° with an inflection point at 350° corresponding to the molecular weight of $FeCO_3$. The final stable residue having the molecular weight of FeO was obtained at 520°.

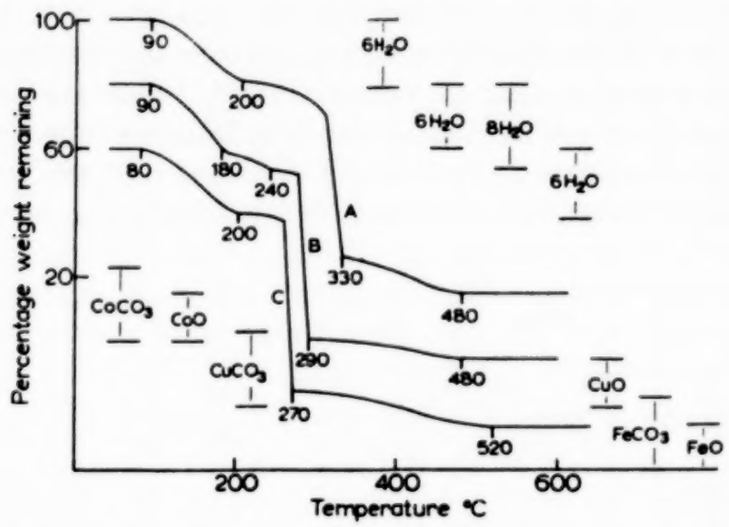

Fig. 2. Thermal decomposition curves. A, Cobalt(II) dilituratе, 335.7 mg heated at 300°/h; B, Copper dilituratе, 323.1 mg heated at 300°/h; C, Iron(II) dilituratе, 273.1 mg heated at 300°/h.

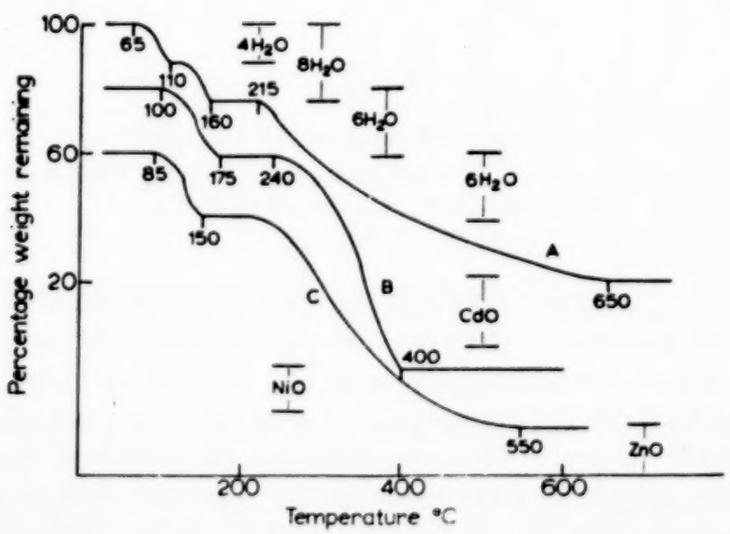

Fig. 3. Thermal decomposition curves. A, Cadmium dilituratе, 40.5 mg heated at 150°/h; B, Nickel dilituratе, 185.6 mg heated at 150°/h; C, Zinc dilituratе, 282.6 mg heated at 65°/h.

Cobalt(II) dilituratе. Cobalt(II) dilituratе formed an hexahydrate stable to 90°. A one-step dehydration followed terminating at 200°. The anhydrous compound was stable to 230°. An explosion, milder than in the case of iron(II) dilituratе, took place to 330° followed by a decomposition with a S-shaped curve giving a residue with a molecular weight corresponding to CoO at 480°. No inflection appeared for an apparent molecular weight corresponding to $CoCO_3$.

Nickel dilituratе. Nickel dilituratе formed also an hexahydrate stable to 100°. Dehydration took place between 100° and 175° with the resulting anhydrous compound being stable to 240°. A rapid one-step decomposition followed to 400° giving a residue, the molecular weight of which corresponded to NiO.

Copper dilituratе. Copper dilituratе octahydrate when decomposed at the rate of heating of 300°/h (Fig. 2) was stable to 90° but neither the dihydrate nor the anhydrous forms had any degree of stability. They appeared only as inflection points at 180° and 240° respectively. A very fast decomposition, with explosion, followed to 290°, continued with a slow decomposition until 480° where a stable residue with a molecular weight corresponding to that of CuO remained. When the rate of heating of 65°/h was used instead of 300°/h (Fig. 4) the dehydration of the octahydrate began at 70°, with the intermediate dihydrate being stable between 115° and 150°, and the anhydrous compound being stable between 180° and 190°.

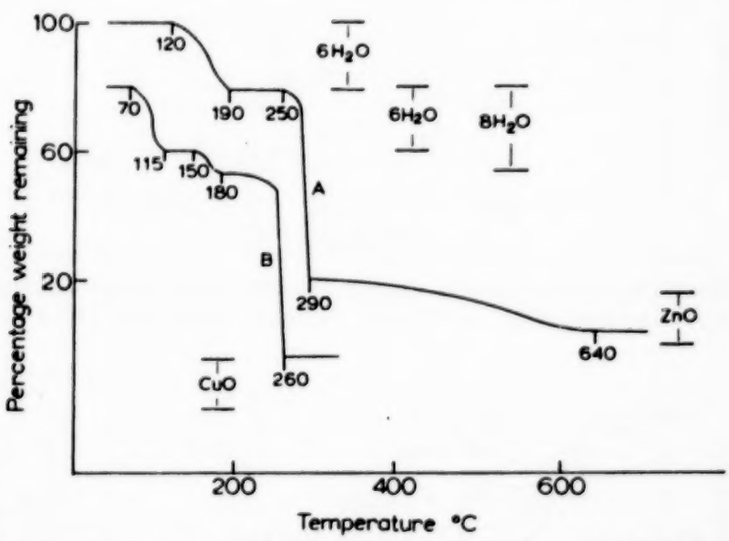

Fig. 4. Thermal decomposition curves. A, Zinc dilituratе, 506.7 mg heated at 300°/h; B, Copper dilituratе, 348.7 mg heated at 65°/h.

Zinc dilituratе. Zinc dilituratе hexahydrate when decomposed at the rate of 300°/h was stable to 120°. A one-step dehydration followed to 190°. The carbon and hydrogen analysis of the hydrated zinc dilituratе seemed to indicate an octahydrate. This can be due to the different modes of drying prior to analysis or thermolysis. The anhydrous compound was stable to 250°. This was followed by a violent explosion at 290°, in which some of the sample was ejected from the crucible, continued by a decomposition with a S-shaped curve giving a stable residue at 640°. When a rate of heating of 65°/h was used (Fig. 3) the hexahydrate was stable only to 85°, and the anhydrous compound was stable from 150° to 200°. The decomposition of the anhydrous compound was slow leaving at 550° a stable residue with a molecular weight corresponding to ZnO.

Cadmium dilituratе. Cadmium dilituratе octahydrate was not very stable. An initial partial dehydration took place between 65° and 110°. The tetrahydrate formed was stable to 120°. A second dehydration followed giving anhydrous cadmium dilituratе stable from 160° to 215°. The decomposition which followed was very slow and gradual, leaving a stable residue at 650° with a molecular weight corresponding to CdO.

MAGNETIC SUSCEPTIBILITY

Two different determinations of the molar paramagnetism of cobalt(II) diliturate hexahydrate gave values of $\chi_M = 7.5 \cdot 10^{-3}$ and $1.02 \cdot 10^{-2}$ corresponding to μ_{eff} of 4.3 and 4.9 respectively. Cobalt(II) diliturate dehydrated at 192° had a $\chi_M = 5.9 \cdot 10^{-3}$ or $\mu_{eff} = 3.8$ and finally a residue from the decomposition of cobalt(II) diliturate at 250° with an apparent molecular weight of 367 had a χ_M of $7.6 \cdot 10^{-3}$ or $\mu_{eff} = 4.3$. Iron(II) diliturate hexahydrate was found to have $\chi_M = 1.03 \cdot 10^{-2}$ or $\mu_{eff} = 5.0$. A $\mu_{eff} = 4.9$ corresponds to four unpaired electrons while $\mu_{eff} = 3.9$ corresponds to three. The values for the effective magnetic moment obtained for cobalt(II) diliturate and its various decomposition products correspond to approximately three unpaired electrons while the value obtained for iron(II) diliturate corresponds to four. Cobalt(II) has three unpaired electrons in the ionic state (seven electrons in the 3d orbital) while iron(II) has four unpaired electrons (six electrons in the 3d orbital). When these electrons are not paired, as is the case for the above compounds, due to the large positive paramagnetism, then there are no 3d orbitals for bond formation (covalent) and the compounds have to be "essentially ionic"[11]. The water molecules do not prevent the formation of chelates since the number of unpaired electrons remains the same for the anhydrous form. The various metal diliturates are true salts.

SUMMARY

The thermolysis curves of the transition metal diliturates as well as those of copper, zinc, cadmium, ammonium and rubidium have been determined. These diliturates with the exception of ammonium and rubidium diliturates form hydrates. The oxides of the corresponding metals are obtained at relatively low temperatures. Magnetic susceptibility measurements show that these compounds are "essentially ionic" salts.

RÉSUMÉ

Les auteurs ont effectué une étude thermogravimétrique de quelques sels minéraux de l'acide diliturique. Les oxydes correspondants se forment à de relativement basses températures. Des mesures de susceptibilité magnétique ont également été effectuées.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die thermische Zersetzung einiger anorganischer Salze der Dilitursäure (Cu, Zn, Cd, NH_4, Rb). Die Oxydbildung tritt bei relativ niederen Temperaturen ein.

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OBSERVATIONS ON THE USE OF AN ANION EXCHANGE RESIN IN THE DETERMINATION OF AMINOBENZOIC ACIDS, AMINOPHENOLS AND SOME RELATED SUBSTANCES IN BIOLOGICAL MATERIALS

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Although sensitive colorimetric procedures exist for the determination of aminophenols and aminobenzoic acids, difficulties generally arise when applied directly to biological materials, *e.g.* urine. Some preliminary form of separation is often a necessity, not only as an aid to concentration but to eliminate interfering substances and the cation-exchange resin (Dowex 50X12) has been used for this purpose[1].

The present paper is concerned with the use of an anion exchange resin (Dowex 1X10) for a similar purpose. Although there have been reports[2–4] concerning its use in some specialised cases, there is little information with regard to its reaction towards the vast number of organic substances that can occur in some biological materials.

EXPERIMENTAL

Preparation of the column

The resin, Dowex 1X10 (200/400 mesh) was contained in a glass tube fitted with a sintered glass base (Quickfit and Quartz Ltd). The weight of resin used was about 30 g and the dimensions of the operational columns were: height 140 mm, diameter 15 mm.

To ensure that the resin was in the chloride form, before use it was washed with *N* hydrochloric acid and then with water until the pH of the eluate was above 3.0.

Operation of the column

The substances under examination were contained in 100 ml of *N* hydrochloric acid because some biological samples may require a preliminary hydrolysis and this is achieved by heating the acidified sample. Before transferring to the column, the pH of the solution was adjusted to 7.0 by the addition of alkali. The column was then washed with 100-ml quantities of water. Elutions were then carried out with 100-ml quantities of *N*, 5 *N* and 8 *N* hydrochloric acid in turn.

Examination of eluates

Identification in eluates was made by colorimetric, fluorimetric or U.V. spectrophotometric methods. The following colorimetric methods were employed in the assessment of substances referred to in Tables II and III:

(*1*) *o*- and *p*-aminobenzoic and *p*-aminohippuric acids, sulphanilic acid and sulphanilamide: diazotisation with nitrous acid followed by coupling with *N*-(1-naphthyl)-ethylenediamine dihydrochloride[1,5,6].

(*2*) *p*-aminophenol: indophenol pigment formation in the presence of *o*-cresol and ammonia[7].

(*3*) 3-hydroxyanthranilic acid: indophenol pigment formation in the presence of 2,6-dichloroquinone chlorimide[7] or molybdenum blue formation[8].

(*4*) *o*-aminophenol: indophenol pigment formation in the presence of 2,6 dichloroquinone chlorimide[7] or molybdenum blue formation[8].

(*5*) nicotinic acid with cyanogen bromide and *p*-aminoacetophenone[9].

RESULTS

Substances representative of the wide variety that may be encountered in biological materials were transferred to the column in quantities of 1, 2, 5 and 10 mg and the results obtained are summarised in Table I.

TABLE I

THE BEHAVIOUR OF SOME SUBSTANCES WHEN PASSED THROUGH A COLUMN CONTAINING DOWEX 1 X10

(1) Substances not retained
Glutamic acid, aspartic acid, asparagine, cystine, taurine, betaine, trigonelline, methionine, hydroxyproline, citrulline, creatinine, α- and β-alanines, creatine, glycine, 3,4-dihydroxyphenylalanine.

(2) Substances partially retained and removed by washing with water
Nicotinamide, kynurenine, 3-hydroxykynurenine, tyrosine, adrenaline, nor-adrenaline, 3-hydroxytyramine, 5-hydroxytryptamine, N_1-methylnicotinamide, morphine, codeine, strychnine, quinidine.

(3) Substances retained and not removed by water; eluted by N hydrochloric acid
Nicotinic acid, *o*- and *p*-aminobenzoic acids, *p*-aminohippuric acid, sulphanilic acid, sulphanilamide, *o*- and *p*-aminophenols, 3-hydroxyanthranilic acid. Uric acid, phosphate, sulphate.

(4) Substances retained and not removed by water or N hydrochloric acid; eluted by 5 N hydrochloric acid
Kynurenic acid.

(5) Substances retained and not removed by water; not eluted by N, 5 N or 8 N hydrochloric acid
Indoleacetic acid, 5-hydroxyindoleacetic acid, caffeic acid, gentisic acid, gallic acid, ferulic acid, vanillic acid, salicylic acid, hippuric acid, xanthurenic acid, barbituric acid. 3,4-dihydroxybenzoic acid, *o*- and *p*-hydroxycinnamic acids. Phenol, catechol, resorcinol, pyrogallol, vanillin, thymol, phloroglucinol, hydroquinone, *o*-, *m*- and *p*-cresols, α- and β-naphthols.

Amino acids showed no evidence of retention whereas phenols and phenolic acids were retained and could not be eluted by hydrochloric acid as concentrated as 8 *N*.

A large group of substances showed evidence of a variable degree of retention by the resin but could be removed by water alone. With the exception of the alkaloids — strychnine, brucine, codeine and quinidine — 200 ml of water was found to be sufficient to remove such retained substances from the column. In the case of the alkaloids, complete removal from the column required a much greater volume of water.

The remaining group, *i.e.* aminophenols, 3-hydroxyanthranilic acid, aminobenzoic acids, nicotinic acid, sulphanilic acid and sulphanilamide, were completely retained by the column and were not removed by water. These substances could be completely eluted by dilute mineral acid, *e.g.* *N* hydrochloric acid.

TABLE II

THE RECOVERY OF SOME ORGANIC SUBSTANCES

(applied to a column of Dowex 1X10 (30 g) in a solution of 100 ml of *N* hydrochloric acid, the pH being adjusted to 7 by the addition of alkali. Elution with 200 ml of *N* hydrochloric acid)

Substance	*Quantities mg*	*Recovery (in 200 ml of N hydrochloric acid eluate) %*
o-aminobenzoic acid	0.5 1.0 2.0	84.5–90.6
p-aminobenzoic acid	0.5 1.0 2.0	86.2–91.6
p-aminohippuric acid	0.5 1.0 2.0	91.6–95.2
o-aminophenol	0.5 1.0 2.0	81.2–86.4
p-aminophenol	0.5 1.0 2.0	82.8–86.2
3-hydroxyanthranilic acid	0.5 1.0 2.0	86.0–89.8
nicotinic acid	0.5 1.0 2.0	83.2–90.2
sulphanilic acid	0.5 1.0 2.0	86.2–94.6
sulphanilamide	0.5 1.0 2.0	87.2–95.8

TABLE III

THE RECOVERY OF SOME ORGANIC SUBSTANCES

(applied to a column of Dowex 1X10 (30 g) in 100 ml of urine + 10 ml of 10 *N* hydrochloric acid, the pH being adjusted to 7 by the addition of alkali. Elution with 200 ml of *N* hydrochloric acid)

Substance	*Quantities mg*	*Recovery (in 200 ml of N hydrochloric acid eluate) %*
o-aminobenzoic acid	0.5[a]	83.8 81.8 86.2
	1.0[a]	87.2 90.6 89.2
	2.0[a]	91.2 95.6 93.2
p-aminobenzoic acid	0.5[a]	88.8 86.2 89.1
	1.0[a]	84.2 83.8 90.2
	2.0[a]	90.8 90.6 96.2
p-aminohippuric acid	0.5[a]	91.2 89.8 88.6
	1.0[a]	88.8 91.2 89.2
	2.0[a]	98.2 96.3 94.2
o-aminophenol	0.5[a]	76.3 79.6 80.2
	1.0[a]	79.6 83.2 84.6
	2.0[a]	81.2 83.6 82.2
p-aminophenol	0.5[a]	81.6 83.3 82.6
	1.0[a]	83.6 81.6 82.8
	2.0[a]	81.6 82.3 83.8
3-hydroxyanthranilic acid	0.5[a]	79.2 77.6 80.6
	1.0[a]	81.2 80.6 80.3
	2.0[a]	83.8 84.2 82.6

TABLE III (continued)

Substance	*Quantities mg*	*Recovery (in 200 ml of N hydrochloric acid eluate) %*
nicotinic acid	0.5[a]	89.3 90.2 89.6
	1.0[a]	87.3 85.8 86.3
	2.0[a]	88.6 89.8 85.3
sulphanilic acid	0.5[a]	95.6 94.2 98.6
	1.0[a]	97.2 96.8 94.2
	2.0[a]	94.6 98.6 97.2
sulphanilamide	0.5[a]	92.3 94.6 98.6
	1.0[a]	96.2 95.3 94.6
	2.0[a]	98.6 92.6 91.8
o-aminobenzoic acid	0.5[b]	89.8 93.6 94.2
	1.0[b]	98.6 94.6 92.6
	2.0[b]	93.2 94.6 93.8
p-aminobenzoic acid	0.5[b]	94.6 95.2 93.8
	1.0[b]	94.8 96.2 97.2
	2.0[b]	96.8 98.2 98.6
p-aminohippuric acid	0.5[b]	94.8 95.2 97.2
	1.0[b]	96.8 95.2 94.2
	2.0[b]	96.8 94.3 97.2
o-aminophenol	0.5[b]	76.3 78.3 77.6
	1.0[b]	81.3 83.8 84.6
	2.0[b]	82.6 83.6 81.3
p-aminophenol	0.5[b]	79.6 77.8 81.1
	1.0[b]	83.2 81.6 87.2
	2.0[b]	86.2 79.2 79.8
3-hydroxyanthranilic acid	0.5[b]	79.3 81.3 80.6
	1.0[b]	79.8 83.8 84.6
	2.0[b]	83.2 84.6 81.0
o-aminophenol	0.5[c]	79.3 78.6 77.7
	1.0[c]	81.6 79.2 83.6
	2.0[c]	80.2 83.6 81.2
p-aminophenol	0.5[c]	81.2 77.3 81.2
	1.0[c]	79.2 79.3 80.2
	2.0[c]	80.8 79.3 81.2
3-hydroxyanthranilic acid	0.5[d]	76.3 77.8 79.2
	1.0[d]	81.3 78.4 76.2
	2.0[d]	82.6 83.8 78.3

[a] No additional treatment

[b] The mixture containing the substance in 100 ml of urine + 10 ml of 10 *N* hydrochloric acid was placed in a boiling water bath for 1 h previous to neutralisation and application to the column.

[c] Previous to quantitative determination, the aminophenols were extracted with ether from the *N* hydrochloric acid eluate after the adjustment of the pH to 7 by the addition of solid sodium bicarbonate[1].

[d] Previous to quantitative determination, 3-hydroxyanthranilic acid was extracted with ether from the *N* hydrochloric acid eluate after the adjustment of the pH to 3 by the addition of a saturated solution of sodium acetate.

The quantitative recovery of *o*- and *p*-aminobenzoic, *p*-aminohippuric, sulphanilic, 3-hydroxyanthranilic and nicotinic acids, *o*- and *p*-aminophenols and sulphanilamide was examined. Such were applied to the column in 100 ml of *N* hydrochloric acid after adjustment to pH 7.0 by the addition of alkali. The column was then washed with 200 ml of water which generally proved sufficient to remove loosely retained substances such as kynurenine. Elution was carried out with *N* hydrochloric acid. A volume of 200 ml proved to be sufficient in every case and the results shown in Table II indicate that recoveries were quantitative.

The above experiments were repeated, the substances being applied to the column in 100 ml of urine. Before application, 10 ml of 10 *N* hydrochloric acid were added and the pH adjusted to 7.0 by the addition of alkali. The results shown in Table IIIa indicate that recoveries were quantitative.

In the case of the aminobenzoic acids and the aminophenols, the mixture of urine and hydrochloric acid was heated in a boiling water bath for 1 h, prior to the column technique. This ensures the hydrolysis of all urinary conjugates with the exception of those containing glycine or glutamine. The results shown in Table IIIb indicate that recoveries were quantitative.

The results shown in Table IIIc and IIId indicate that the aminophenols and 3-hydroxyanthranilic acid can be separated from the acid eluates with ether after adjustment to pH 7 (with sodium bicarbonate), and pH 3 (with sodium acetate) respectively[1]. The eluates were not concentrated before this treatment.

DISCUSSION

In earlier experiments columns containing only 3 g of anion (Dowex 1X10) exchange resin were used. Since it was intended to apply the experimental findings to the examination of urine in 100-ml quantities, a column containing about 30 g of resin was adopted. This has proved more than adequate to cope quantitatively with the wide range and variety of substances likely to be present in this volume of urine.

Although the anion (Dowex 1X10) and cation (Dowex 50X12) exchange resins appear to achieve the same purpose, there are some distinct differences which are advantageous when biological materials are under examination.

The cation exchange resin has been successfully applied to the separation of a variety of substances possessing a basic group from human urine as a preliminary to colorimetric analysis. A column containing about 3 g of resin has been used. 100 ml of urine (+ 10 ml of 10 *N* hydrochloric acid) is applied to the column when examination is limited to those substances requiring hydrochloric acid of a normality greater than 1, for example, kynurenine requires 5 *N* hydrochloric acid, to effect elution. Since many of the commoner 'basic' substances, *e.g.* urea, amino acids, are not retained under such conditions, the capacity of the column is not overtaxed by the use of this large volume of urine. 10 ml of urine diluted to 100 ml with water (+1 ml of 10 *N* hydrochloric acid) is applied to the column when examination is made of those substances requiring hydrochloric acid of a normality of 1 or less to effect elution. The capacity of a column of this size has never been found to be overtaxed when the quantity of urine used has been limited to this volume. A column of large size could be used and a larger volume of urine applied but the advantage is negatived by a larger volume of eluant which requires concentration.

After the application of 100 ml of urine to the anion exchange resin, 3-hydroxy-

anthranilic acid and aminophenols may be recovered in 200 ml of *N* hydrochloric acid eluate. Such represents a relatively slight dilution and the above substances can be recovered by ether extraction (at pH 3 and 7 respectively), concentration of the aqueous phase not being necessary. Eluates obtained from the cation exchange resin are much more dilute and some concentration is necessary before ether extraction is attempted.

The use of the anion exchange resin allows of a speedier separation of these substances from a crude material such as urine. Some *o*-hydroxyamines, *e.g.* 3-hydroxyanthranilic acid, have been shown to be carcinogenic in the free but not in the conjugated form. Since urine is applied to the anion exchange resin at a neutral reaction and elution is speedier, the separation of these two forms is achieved with less risk of hydrolysis of the conjugated form.

The anion exchange resin offers similar advantages to the determination of the aminobenzoic acids in urine. Elution is speedier and eluates are sufficiently concentrated to allow direct determination.

Sulphonamides, if present, would be included but these are not normal constituents of urine. Aminohippuric acids are included but these are minor constituents. Actually a more effective separation of these substances can be achieved by means of the cation exchange resin.

The resolution of the eluate obtained from the anion exchange resin upon the cation exchange resin may be an advantage in many cases.

The separation of alkaloids from acidic radicles by means of the anion exchange resin does not appear to be a practical proposition due to retention problems. Nicotinamide and nicotinic acid may be separated if required. The separation of morphine from *p*-aminophenol, a metabolite of phenacetin, appears to be a practical proposition. This would be of value in toxicological analysis since *p*-aminophenol can seriously interfere with the detection and determination of morphine, and there are relatively few methods for their separation.

SUMMARY

An anion exchange resin (Dowex 1X10) has been studied for the purpose of separating aminobenzoic acids, aminophenols, sulphanilamide and nicotinic acid, preparatory to their determination by colorimetric methods.

RÉSUMÉ

La résine Dowex 1X10 a été examinée en vue de la séparation des acides aminobenzoïques, aminophénols, sulfanilamide et acide nicotinique dans des substances biologiques.

ZUSAMMENFASSUNG

Untersuchung über die Eignung eines Jonenaustauschers zur Trennung von Aminobenzoesäuren, Aminophenole, Sulfanilamid und Nikotinsäure.

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CHROMATOGRAPHIC SEPARATION OF IONS IN PRESENCE OF OXALATE, TARTRATE AND CITRATE, WITH AQUEOUS ETHANOL AS SOLVENT

PART I

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It is well known that complex formation plays an important role in the separation of ions in chromatography. Various workers, including BURSTALL *et al.*[1] and LEDERER AND LEDERER[2], have studied the separation of inorganic ions by paper chromatography using different solvent mixtures with complexing agents. In previous publications[3,4] we have reported studies on the separation of various metal ions in the presence of varying concentrations of complexing agents, with aqueous alcohols as solvent. In this paper we have extended the work to cover the separation of mixtures of 3, 4 or 5 ions and have employed complex formation with oxalate, tartrate and citrate for the separation of ions by ascending filter paper strip chromatography, with aqueous ethanol as solvent.

EXPERIMENTAL

Standard solutions of silver nitrate, lead nitrate, mercurous nitrate, copper nitrate, mercuric nitrate, bismuth nitrate, cadmium nitrate, cobalt nitrate, tin chloride, antimony chloride, arsenic chloride, potassium oxalate, sodium citrate and sodium tartrate were prepared from reagent grade chemicals. The method adopted was the strip filter paper chromatographic technique, as described by GAGE, DOUGLASS AND WENDER[5]. Various concentrations of aqueous ethanol were tried and it was found that 60% ethanol was suitable as solvent. A series of mixtures containing equal concentrations of metal solutions with varying proportions of the complexing agent were prepared, keeping the total volume constant. The ratio of the total molar concentration of the metals to the concentration of the complexing agent added has been expressed as the metal: complexing agent ratio (equivalents of the complexing agent). The mixtures were spotted on Whatman filter paper No. 1 strips. The chromatograms were run at a constant temperature in a room maintained at 27°, the time allowed being 90 min. In mixtures of 3, 4 and 5 ions, the final concentration of each of the metal ions was 0.033 *M*, 0.025 *M* and 0.01 *M* respectively. Mixtures of various metal ions were investigated. The results obtained are summarised in the Table I.

When complexing agents were added, distinct separation zones were obtained, whereas in the absence of complexants the zones were not well-defined. The results

TABLE I

No.	System investigated (Sequence of separation without adding complexing agents)	Complexing agents added (equiv. up to which separation is possible)			Sequence of separation (complexing agents added)
		Oxalate	Tartrate	Citrate	
1	Pb(II)–Ag(I)–Hg(I)	0.95	0.95	0.70	Pb(II)–Ag(I)–Hg(I)
2	Cd(II)–Hg(II)–Pb(II)	0.32	0.32	0.32	Cd(II)–Hg(II)–Pb(II)
3	Cd(II)–Cu(II)–Pb(II)	0.35	0.35	0.48	Cd(II)–Cu(II)–Pb(II)
4	Cd(II)–Cu(II)–Hg(II)	0.32	0.48	0.48	Cd(II)–Cu(II)–Hg(II)
		—	—	0.8–1.3	Cu(II)–Hg(II)–Cd(II)
5	Cu(II)–Hg(II)–Pb(II)	0.95	0.97	0.97	Cu(II)–Hg(II)–Pb(II)
6	Cd(II)–Cu(II)–Bi(III)	0.35	0.38	0.38	Cd(II)–Cu(II)–Bi(III)
7	Cd(II)–Pb(II)–Bi(III)	0.32	0.32	0.32	Cd(II)–Pb(II)–Bi(III)
8	Cd(II)–Cu(II)–Hg(II)–Pb(II)	0.26	0.24	0.24	Cd(II)–Cu(II)–Hg(II)–Pb(II)
9	Co(II)–Cd(II)–Cu(II)–Hg(II)–Pb(II)	0.50	0.30	0.30	Co(II)–Cd(II)–Cu(II)–Hg(II)–Pb(II)
10	Sn(II)–Sb(III)–As(III)	—	—	0.64	Sn(II)–Sb(III)–As(III)
		0.64–0.96	0.16–0.64	—	Sn(II)–As(III)–Sb(III)

suggest that the complexing property of the ions may be useful in the qualitative separation of these ions from their mixtures. With higher concentrations of the complexing agent than those mentioned, separation is not possible under the experimental conditions. The complexing agent was added to the solution of the metals and not to the solvent as was usually done by previous workers.

SUMMARY

The paper chromatographic separation of Ag, Hg, Pb, Bi, Cu, Cd, Co, As(III), Sb(III) and Sn(II) in mixtures of 3, 4 or 5 of these ions has been studied in the absence and presence of oxalate, citrate and tartrate with aqueous ethanol as solvent.

RÉSUMÉ

Les auteurs ont effectué une étude sur la séparation chromatographique des cations suivants: Ag, Hg, Pb, Bi, Cu, Cd, Co, As(III), Sb(III) et Sn(II). Ils ont examiné également l'influence de réactifs complexants (oxalate, citrate et tartrate).

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Trennung von Ag, Hg, Pb, Bi, Cu, Cd, Co, As(III), Sb(III) und Sn(II) durch Papierchromatographie sowie über den Einfluss von Komplexbildnern auf die Trennung.

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QUANTITATIVE CHROMATOGRAPHIC ANALYSIS USING RECTIFIED RADIO-FREQUENCY METHODS

I. LITHIUM, SODIUM AND POTASSIUM

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INTRODUCTION

A series of papers by BLAKE has appeared in this journal in recent years in which a rectified radio-frequency apparatus is described for the detection of spots of electrolyte on chromatography paper. Using this apparatus, which he called "G. G. Blake's Rectified Radio-Frequency Chromatograph Zone Localizer", and which will be referred to henceforth as the "zone detector", he showed that if the galvanometer response be plotted (on the y-axis) against the distance along the paper strip (on the x-axis), then the area under the resultant curve (which he called the "R.Rf. solute distribution/current graph" and which will be referred to as the "detector curve" in this paper) was independent of the shape or area of the spot of electrolyte, but bore a quantitative relationship to the mass of electrolyte[1]. This observation led the present authors to investigate the feasibility of using BLAKE's apparatus for the quantitative determination of spots of ions which had actually been separated by paper chromatography. As the ion spot was in no way changed by the apparatus, the method offered obvious advantages where the separated ions were required for recovery and/or further investigation.

EXPERIMENTAL

Preliminary investigation of several different groups of metal ions showed that where a non-conducting organic solvent mixture was used to develop the chromatogram, a detector curve was obtained in which the background was low and uniform, so that the area of the detector curve corresponding to each ion spot could be determined satisfactorily. On the other hand, when the chromatogram was developed by a solvent mixture containing a conducting compound such as hydrochloric or acetic acid, a detector curve was obtained in which the ion spot curves were superimposed on high and variable backgrounds. Despite all efforts to eliminate this background by heating the developed paper chromatograph in an electric oven or by infra-red lamp, it could not be appreciably reduced, and it was concluded that it was due to a change in the paper itself. Accordingly, it was decided to concentrate further work on the alkali chlorides, which could be separated by non-conducting solvent mixtures.

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Although several different developing mixtures have been described for the chromatographic separation of the alkali chlorides[2,3], none of these was found to give complete separation, and a new mixture was developed for this purpose. This mixture, 3 : 7 (by volume) 2-ethyl hexanol/methanol, gave satisfactory separation of lithium, sodium and potassium chlorides, and was used in all further work. The R_f values for these ions were: $Li^+ = 0.65 \pm 0.04$; $Na^+ = 0.21 \pm 0.03$; $K^+ = 0.06 \pm 0.03$.

Initial quantitative measurements on chromatographs confirmed that the areas under the detector curve for a series of ion spots were proportional to the masses of the respective ions when measured at the same time. However, the same quantity of, say, sodium chloride, gave different detector curve areas on different days, and it was readily established that this variation was dependant on the relative humidity of the atmosphere (Fig. 1). It was therefore clear that although the "zone detector" was very suitable for the determination of the position and limits of chromatograph spots, it could not by itself be used for their quantitative measurement unless ambient humidity were strictly controlled. As this condition was not a practicable one, it was decided to detect and measure the chromatograph spots in two separate steps.

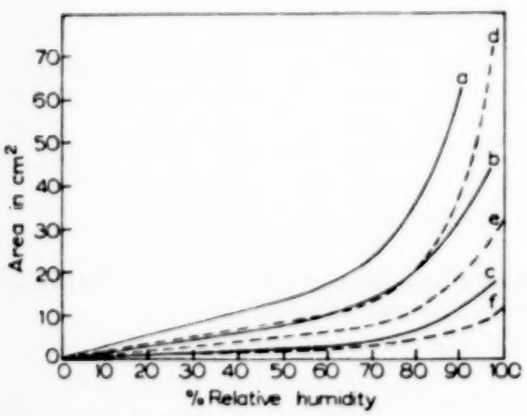

Fig. 1. Dependence of detector curve area on relative humidity of atmosphere. Curves a, b, c: NaCl; 1.09, 0.55, 0.11 mg of Na^+. Curves d, e, f: KCl; 1.09, 0.55, 0.11 mg of K^+.

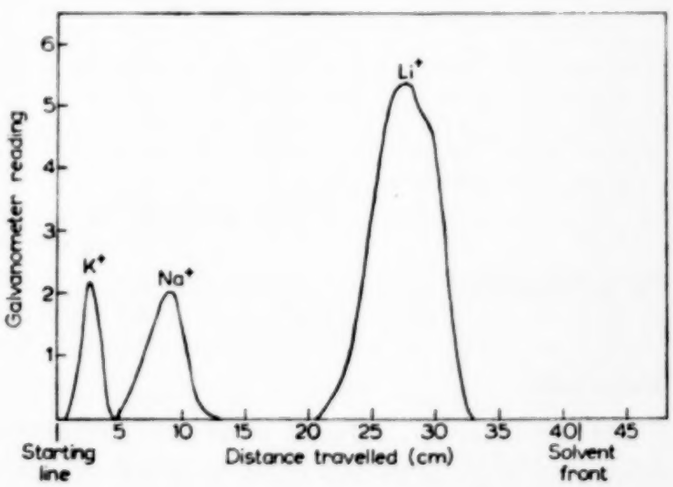

Fig. 2. Typical zone detector curve of mixed potassium, sodium and lithium chlorides.

The position of the ion bands were first determined with the zone detector[4,5], a typical curve thus found being shown (Fig. 2). The bands were then cut out and extracted with a known quantity of distilled water. The impedances of the resulting solutions were measured in a conductimetric tube[4,6], at constant temperature and the mass of the ion found from a calibration curve of Solution impedance/Ion concentration for that particular ion (Fig. 3).

The determination of the quantity of alkali metal ions by this method was convenient, since the apparatus of the zone detector could be used merely by substituting a different electrode system. It should be noted, however, that the zone detector placed no constraint at all on the method of determination of the quantity of ions in the zones it detected. Thus spots of easily hydrolysed ions could be first located by the zone detector, then extracted with dilute acid and determined, say, colorimetrically

or by chelometric titration. It would moreover appear that the earlier difficulty encountered, *i.e.* the high and variable background of the detector curve obtained when the chromatogram was developed with a solution containing hydrochloric or acetic acid, should be overcome by the separation of detection and measurement of the ion spots into two independent steps, unless the quantity of ion in a spot were too small for identification against the background.

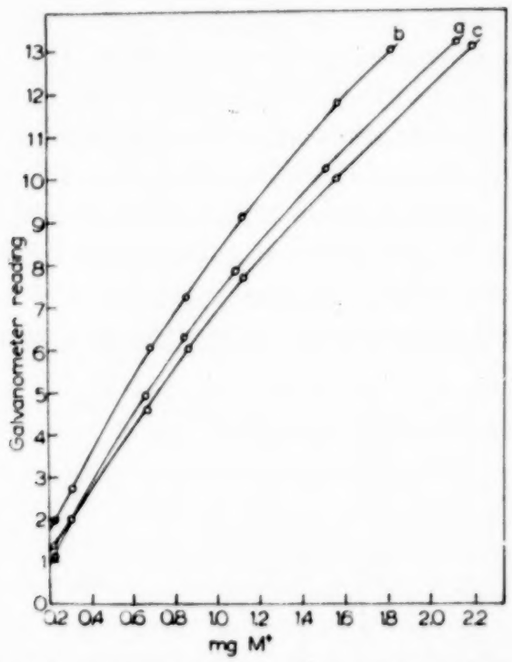

Fig. 3. Calibration curves of solution impedance at 20° plotted against ion concentration. Curve a: Li^+ in 85 ml; curve b: Na^+ in 25 ml; curve c: K^+ in 20 ml.

Materials

Sodium chloride: 1.74 *M* solution (contained 40 mg Na^+ per ml). A.R. NaCl was dried and the calculated mass weighed out and dissolved.

Potassium chloride: 1.023 *M* solution (contained 40 mg K^+ per ml). A.R. KCl was dried and the calculated mass weighed out and dissolved.

Lithium chloride: The lithium chloride was weighed as the monohydrate, dissolved, and standardised against standard silver nitrate. It was found to be 5.595 *M*, *i.e.* 38.8 mg of Li^+ per ml.

Twice-distilled water was used in all cases.

Chromatography paper: Whatman No. 3 chromatography paper gave the best separation. The strips were 5 cm wide and slightly more than 50 cm long. Where less than 1 mg of metal ion was present, strips 2.5 cm wide proved satisfactory.

Developing solvent: This was a 3 : 7 (by volume) mixture of 2-ethyl-hexanol and methanol, and was used without special purification.

The galvanometer used with the zone locator and conductimetric tube was a Pye "Scalamp" galvanometer of sensitivity 177 mm/μA. The results in Table I were obtained using a sensitivity setting of *X* 0.01, (*i.e.* 1.77 mm/μA).

PROCEDURE

The metal chloride solutions were placed on a pencil line about 3 cm from one end

of each strip of paper and dried. The small volumes required were obtained by using calibrated capillary tubes whose volumes covered the range 8 to 55 μl. For each volume, sixteen chromatograms were prepared, consisting of four of the mixed alkali chlorides and four each of the individual alkali chlorides to provide the standards for the calibration curves. The samples were then chromatographed by upward development for 24 h in large glass tanks. Care was taken to prevent the papers from touching whilst in the tank and afterwards while drying.

TABLE I

(Each result is the mean of four to six separate chromatograms)

Metal	*Mixture No.*	*Vol. of water extract (ml)*	*Mean galv. reading (cm)*	*Max. deviation (cm)*	*mg Li^+ present*	*mg Li^+ found*	*Error (%)*
Li^+	1	85	13.02	0.08	2.13	2.12	— 1
	2	85	10.18	0.12	1.52	1.52	< 1
	3	85	7.85	0.25	1.20	1.20	< 1
	4	85	6.36	0.04	0.84	0.86	+ 2
	5	85	5.05	0.05	0.67	0.68	+ 1
	6	85	2.05	0.20	0.30	0.30	< 1
	7	85	1.12	0.02	0.21	0.21	< 1
Na^+	1	25	12.70	0.05	1.83	1.80	— 2
	2	25	11.63	0.15	1.57	1.57	< 1
	3	25	9.13	0.18	1.13	1.14	+ 1
	4	25	7.43	0.20	0.87	0.88	+ 1
	5	25	6.19	0.10	0.69	0.71	+ 3
	6	25	3.03	0.30	0.31	0.34	+10
	7	25	2.08	0.38	0.22	0.23	+ 5
K^+	1	20	12.89	0.04	2.19	2.19	< 1
	2	20	10.08	0.20	1.57	1.60	+ 2
	3	20	7.40	0.20	1.13	1.09	— 4
	4	20	6.06	0.16	0.87	0.87	< 1
	5	20	4.72	0.22	0.69	0.68	+ 2
	6	20	2.13	0.17	0.31	0.32	+ 3
	7	20	1.14	0.11	0.22	0.20	—10

The chromatograms were dried thoroughly to remove the developing solvent, as traces of solvent caused irregularities in the detector curve and errors in the impedance measurements. The dried chromatograms were next conditioned for an hour in a tank of about 90% relative humidity, to increase the effective sensitivity of the zone detector. After the separated ion zones were located by the zone detector, they were cut out with scissors, cut into smaller pieces and placed in dry 100-ml conical flasks. The requisite amount of distilled water was then pipetted in; this amount varied for each of the alkali metals, but was initially found by experiment so that the galvanometer readings were on the scale. It is recommended that the volume be not less than 20 ml.

The flasks were then well shaken and placed in the constant temperature bath ($20 \pm 0.3^\circ$), as the solution impedance varied measurably with temperature. When they had reached the temperature of the bath, they were quickly removed and the impedances of the solutions measured with the conductimetric tube, the galvanometer having been first set to zero for distilled water. The mass of metal ion present was then read from a calibration curve prepared in a similar manner.

The results of analysis of the alkali chloride mixtures are given in Table I, and the calibration curves in Fig. 3.

The upper limit of the range of the method was found to be approximately 2 mg of M^+; larger quantities could not be completely separated on the strips of chromatographic paper used. The lower limit of the range was set by the limit of detection of the zone detector; this was found to be 10 μg for K^+ and 200 μg for Li^+ and Na^+, the difference being due to the fact that the K^+ zone was much less spread out than the others. Within these limits the accuracy of the method may be given as

Li^+, 0.2–2 mg with an accuracy of 1%
Na^+, 0.7–2 mg with an accuracy of 1%
K^+, 0.7–2 mg with an accuracy of 2%.

The accuracy is greatest for Li^+ as the impedance measurements depend on the ionic strength of the solution, which will naturally be the greatest for Li for a given number of mg.

Throughout the work, the solvent front was allowed to travel about 48 cm; it was found that a solvent front movement of 42 cm was necessary to effect complete separation.

Semi-quantitative estimation of μg quantities of the metals could be achieved by running simultaneous reference chromatograms of mg quantities, then cutting out portions of the test chromatograph corresponding to the zones detected on the reference chromatograph. The impedance of the aqueous extract was measured as usual, but with the galvanometer on a five times more sensitive setting. Errors were naturally large, being of the order Na^+, 10%; Li^+, 20%; K^+, 30%.

ACKNOWLEDGEMENT

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SUMMARY

The BLAKE Zone Detector has been shown to be a very useful apparatus for the location of ion zones separated by paper chromatography. In the case of the alkali metals, these zones can be estimated by measuring the impedance of their aqueous extract. An alternative method, that of measuring the area under the detector curve, does not provide a practical means of quantitative measurement. A new developing solvent is described for the paper chromatographic separation of lithium, sodium and potassium chlorides.

RÉSUMÉ

Les auteurs ont étudié la séparation chromatographique sur papier des métaux alcalins (LiCl, NaCl et KCl), en utilisant avec succès l'appareil de BLAKE pour la localisation des zones.

ZUSAMMENFASSUNG

Beschreibung einer papierchromatographischen Trennung der Alkalimetalle unter Verwendung des Apparates nach BLAKE zur Lokalisierung der Zonen.

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DETERMINATION OF LEAD IN GASOLINE BY ATOMIC ABSORPTION SPECTROSCOPY

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The determination of lead in gasoline is one which is carried out with great frequency by the petroleum refining industry. The lead content of a gasoline has a very important modifying effect upon the octane value of that gasoline. There is, therefore, no necessity to point out the importance of this determination, both to the producer and to the consumer of this fuel.

As with most methods of analysis, the most important criteria of the procedure are the accuracy and precision, ease of manipulation, speed of carrying out the procedure, and the degree of interference from other elements or compounds likely to be present in the system. The most commonly used methods for this determination are wet chemical analysis, X-ray fluorescence, and flame photometry. In the *wet chemical procedure* the sample is digested and decomposed with acid. The lead is converted to the sulfate and is determined gravimetrically as lead sulfate. This procedure is quite accurate but is time-consuming and requires considerable attention.

X-Ray fluorescence

The advantage of this procedure is that it is very rapid and requires a minimum of preparation of the sample[1]. Its disadvantages lie in the fact that it is costly to install, and subject to errors from variations in the sample. These variations include carbon/hydrogen ratio and sulfur content.

Flame photometry

The flame photometric procedure is rapid and easy to carry out. However, some interference might be expected from change in concentration of the other trace elements present in the sample.

The atomic absorption procedure possesses all the required advantages described earlier, *i.e.*, a minimum of preparation of the sample is required; time for complete analysis, including calculation, is approximately 10 min, the equipment is relatively cheap. Accuracy of the results obtained show that the method is quite reliable and reproducible. Also, the procedure is remarkably free from interference from other elements present; sulfur and nitrogen content in the sample and variation in the carbon/hydrogen ratio caused no interference at the levels normally encountered. Also, the method enjoyed freedom from interference from metals normally encountered in this type of sample.

DISCUSSION

The process of atomic absorption spectroscopy was first demonstrated by WALSH[2]. The principle of the procedure is that metal atoms will absorb at certain well-defined, characteristic wavelengths. This absorption is intense and permits analyses to be carried in the p.p.m. level. The principle advantages of the procedure are *(1)* high degree of sensitivity, *(2)* high degree of freedom from interference by other metals. A schematic diagram of the equipment used for this process is shown in Fig. 1.

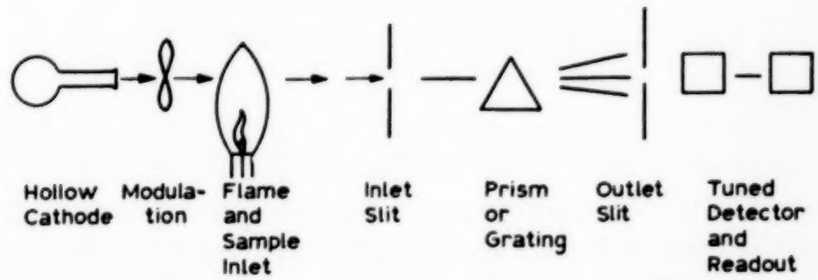

Fig. 1. Schematic diagram of atomic absorption spectrophotometer.

RESULTS

It was determined that lead absorbed strongly at wavelength 2833 Å. At this wavelength the degree of absorption was so intense that the useful range of analysis was limited to between 0 and approximately 70 p.p.m. of lead*. At greater concentrations of lead, the relation between concentration and degree of absorption was on the flat part of the calibration curve and useful analytical results were difficult to obtain. This is shown in the calibration data which illustrate the relationship between concentration of lead and degree of absorption. The results are plotted using the Ringbom relation $K(1 - I_1/I_0) = \log C$. Assuming I_0 is constant, this can be reduced to

$$\log C = K'(I_0 - I_1)$$

where $K = K'I_0$
C = Concentration of metal
I_0 = Intensity of initial signal
I_1 = Intensity of signal after absorption

The most satisfactory working range is between 0 and 70 p.p.m. of lead. To accommodate this limited range, it was necessary to dilute all samples ten-fold. For this dilution, iso-octane was used. Although this dilution necessitated an extra step in the procedure, it had the advantage of virtually standardizing the matrix for all samples. Precision results are shown in Table I.

Interference studies

Solutions were made up to contain 10 p.p.m. of lead and 900 p.p.m. of the metal being studied. Of the following metals examined, no interference was noted. The metals studied were tin, sodium, bismuth, copper, zinc, chromium, iron, and nickel.

Interference from sulfur and nitrogen

The sulfur and nitrogen content of gasoline vary significantly, depending on the

* 1 ml TEL./gal. = 108 p.p.m. Pb, approximately.

TABLE I

PRECISION RESULTS

Lead conc.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
Standard	50	130	220	325	650
Analysis	49.5	128	227	335	647
	49.5	129	219	321	655
	48.5	128	223	321	647
	49.5	129	219	328	655
	50.5	131	219	320	650
	51.0	129	216	320	655
	50.5	130	221	320	650
	50.5	131	221	320	650
		131	217	335	647
		130	216	328	647
		131	217		647
Average	49.4	129.7	219.5	324.5	650.0
	$2\sigma = 1.64$	$2\sigma = 2.5$	$2\sigma = 6.8$	$2\sigma = 13.0$	$2\sigma = 7.0$

source of the crude oil. It was therefore decided to study these elements when present in a high concentration. With sulfur, the compounds carbon disulfide, orthothiocresol, $CH_3C_6H_4SH$, and *n*-butyldisulfide, $C_4H_9SSC_4H_9$, were studied as possible interfering compounds. Diethylamine, $(C_2H_5)_2NH$, was used as the source of nitrogen. To study the effect of interference, an equal quantity of gasoline and possible interfering compound were taken and shaken well. These were then diluted ten-fold and the apparent lead concentration determined. The results are shown in Table II.

TABLE II

INTERFERENCE BY SULFUR AND NITROGEN ON LEAD DETERMINATION

Lead standard p.p.m.	*Apparent analyses interfering compound*		
	Carbon disulfide p.p.m.	*Thiocresol p.p.m.*	*Diethylamine p.p.m.*
50	50	51	51
125	127	127	123
220	220	220	220
325	325	320	330

Sample contained 50% interfering compound, 50% standard. This mixture was diluted ten-fold with iso-octane.

As shown in Table II, there appeared to be no interference from sulfur or nitrogen compounds, even though the compounds were present in an equal volume to gasoline. It is felt that if these elements do not interfere at these high concentrations, they would not interfere at the lower concentrations normally encountered in gasoline analysis. It was concluded, therefore, that the method was free from interference from sulfur and nitrogen. Other studies indicated freedom from interference from halides providing precipitation of the lead did not occur.

EXPERIMENTAL

A schematic diagram of the equipment used is shown in Fig. 1. It was found necessary

to include modulation in this equipment in order to eliminate difficulties arising from the emission line of lead which occurs at the same wavelength as the absorption line. Without modulation, the net absorption as detected by the photomultiplier would be subject to the errors present in emission flame photometry.

Source

A lead hollow cathode was used as the source. Its construction is illustrated in Fig. 2.

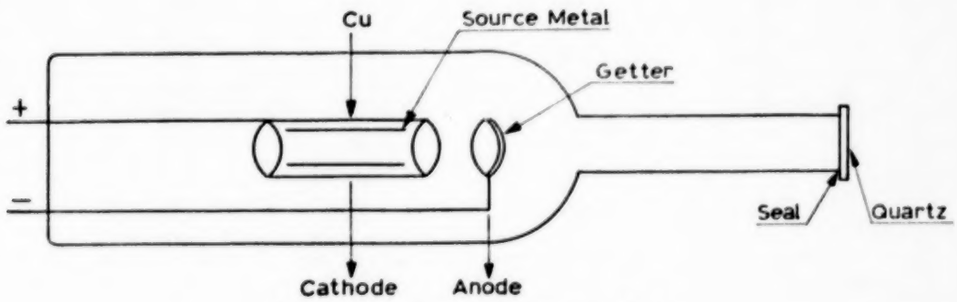

Fig. 2. Design of hollow cathode.

Burner

A standard Beckman flame atomizer burner was used in all cases. The flame was a simple oxy–hydrogen flame.

Monochromator, detector and readout system

A modified Perkin-Elmer Model 13 spectrophotometer was used for this work. Modifications included a chopper operating a 12 cycles/sec and a grating instead of a prism. Although the use of this instrument was quite successful for this application, it is likely that a much simpler instrument embodying modulation of the source and the detector would be quite satisfactory.

PROCEDURE

Calibration

Standard solutions of lead tetraethyl are made up by dissolving in iso-octane. These solutions are prepared to cover the range 0–65 p.p.m. of lead. It is preferable that the standard lead should be in the same form as the sample since different organic compounds of lead may result in a different absorption coefficient and therefore a standard calibration curve may result which would not apply to the samples. The monochromator and detector system are set to read the intensity of the emission line at 2883 Å emitted by the hollow cathode. The unabsorbed signal from the hollow cathode is set to read 100. The source is then shut off, and zero signal is set to read 0. The standard solutions are then aspirated into the Beckman burner in the same way as in flame photometry. The absorption reading, $I_0 - I_1$, is then recorded and plotted in a Ringbom plot where concentration is plotted against $(I_0 - I_1)$, as illustrated in Fig. 3.

Determination of samples

The sample is shaken and 1 ml is accurately pipetted out and placed into a 10-ml graduated flask. Iso-octane (9 ml) is then added until the solution reaches the mark.

The mixture is then well shaken, and the sample poured out and aspirated in the normal way.

The concentration of lead is calculated from the absorbed signal and the calibration curve after suitable correction for dilution.

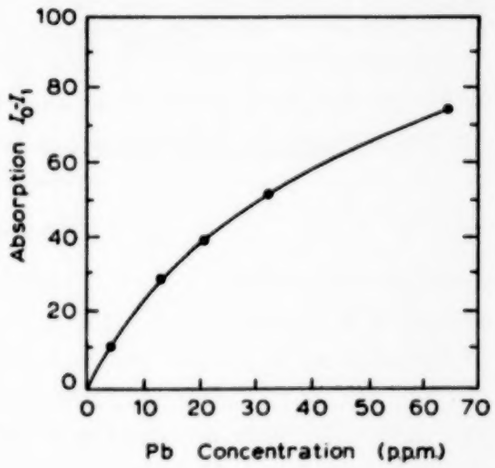

Fig. 3. Calibration curve. Pb concentration (p.p.m.) *vs.* absorption ($I_0 - I_1$).

For subsequent analyses, it must be remembered to set I_0 and zero on the same position on the recorder. This is best accomplished by varying the sensitivity of the detector or the slit widths of the monochromator. For reproducible results it is best not to vary the amperage across the hollow cathode source because of the time necessary to re-attain equilibrium. As a further check a standard solution should be run immediately before a batch of samples requiring analysis. In all cases, a blank should be obtained by running iso-octane alone, and this should be subtracted from the final results.

ACKNOWLEDGEMENTS

The author wishes to thank Esso Standard, Division of Humble Oil & Refining Company, for permission to publish this work.

SUMMARY

A procedure has been developed for the direct determination of lead in gasoline by atomic absorption spectroscopy. This procedure is rapid, does not require expensive equipment, is remarkably free from interference by other trace elements present, and allows considerable variation in the sulfur and nitrogen content of the gasoline. It compares favorably with other existing procedures for this determination, such as X-ray fluorescence, wet chemical methods, and flame photometry.

RÉSUMÉ

Une méthode par spectroscopie d'absorption atomique a été mise au point pour le dosage du plomb dans la gazoline. Ce procédé est rapide; il ne nécessite pas d'appareillage coûteux et il est remarquablement sélectif.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur direkten Bestimmung von Blei in Gasolin durch atomare Absorptionsspektroskopie. Die Methode ist rasch und selektiv.

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THE DETERMINATION OF INDIUM AND THALLIUM IN SILICATE ROCKS BY A COMBINED SOLVENT EXTRACTION AND SPECTROCHEMICAL TECHNIQUE

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INTRODUCTION

The determination of elements of low abundance in geological materials is of considerable interest in geochemistry particularly in those cases (*i.e.* Bi, Tl, Cd, In, etc.) where the concentrations are so low that quantitative determinations are rendered extremely difficult. This problem has to some extent been solved in recent years by the use of neutron activation methods where certain elements can be determined at extremely low concentration levels. A contribution has also been made by the development of techniques depending on the enrichment of elements to the threshold of spectral sensitivity by means of ion exchange followed by spectrochemical analysis. The author has been particularly concerned with the development of anion exchange enrichment techniques, and elements such as Cd, Bi, Tl, Sn, Zn, etc. have been determined in a wide range of geological materials[1–4].

There is however, clearly a place for other methods of separation and enrichment and as has been suggested by SMALES AND WAGER[5] the use of solvent extraction for the solution of the problem is of obvious importance.

In considering methods suitable for the determination of elements at extremely low concentrations in silicate rocks there are certain overriding limitations that must be considered. Of these, by far the most important is that any such method must involve the addition of as few reagents as possible and these reagents must not only be employed in the minimum quantities but must also be easily purifiable, otherwise there is a significant risk of contamination. The author has therefore developed a solvent extraction technique which incorporates simplicity and speed of application with the utmost economy of reagents which are in any case easily purifiable.

IRVING AND ROSSOTTI[6] have investigated the iodo-complexes of the Group IIIb elements and have shown that Tl and In may be extracted quantitatively into ethyl ether from a solution of 1.5 *N* sulphuric acid and 1.5 *N* potassium iodide where the hydriodic acid is generated *in situ*. They do not recommend the use of hydriodic acid itself due to its inherent instability. This extraction procedure is however unsuitable for the determination of In and Tl in silicate rocks owing to two factors. Firstly, it has been discovered that even the purest grade of potassium iodide contains significant amounts of Tl, and secondly, it is not easy to obtain a solution of a silicate rock in sulphuric

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acid owing to the formation of insoluble sulphates. A modified procedure was therefore developed in which the rock specimens were finally dissolved in a mixture of 15% (1.7 *N*) hydrochloric acid to which was added sufficient hydriodic acid to make the solution 1.0 *N* with respect to the latter. It was easy to obtain a solution of the rock in this mixture and moreover the reagents were found to be entirely free of In and Tl. These elements were subsequently determined in a suite of eight rocks including the well-known standard granite G-1 and standard diabase W-1 (see FAIRBAIRN *et al.*[7]). Good agreement was obtained not only with the results of other workers for these standard rocks but also with the author's previous work on anion exchange enrichment.

APPARATUS

The spectrochemical determinations were carried out on a large Hilger quartz/glass spectrograph in which the discharge was focussed on the slit by means of a Hilger E 958 quartz lens. A rotating step sector with a transmission ratio of two served to provide a graded series of exposures and the spectra were recorded on Kodak 103–0 blue-sensitive plates in the range 2750 Å to 4680 Å.

EXPERIMENTAL TECHNIQUE

Spectrographic procedure

Since the amounts of the ethereal residues which were to be analysed spectrochemically were exceedingly low (about 5 mg), some form of matrix was necessary to

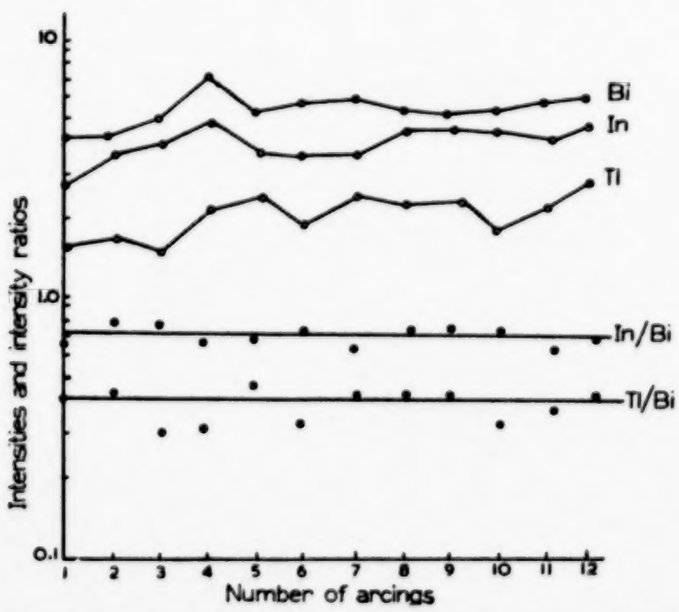

Fig. 1. Replicate arcings of small amounts of Bi, In and Tl showing the efficacy of Bi as internal standard.

collect the residues and to afford sufficient bulk. Sodium chloride was found to be particularly suitable for this purpose since it not only is readily obtainable in a high degree of purity but also has the property of quenching CN emission during arcing, and hence reduces CN band interference[8] in the region of the most sensitive Tl line at 3775 Å. A further advantage of this matrix is that In, Tl and Bi (the internal standard) are all volatilised by the time that the sodium "D" colour has started to

wane and cutting off the exposure at this point eliminates much interference from the less volatile elements such as Fe.

A series of volatilisation tests were carried out with various volatile elements conjointly with In and Tl in order to choose a suitable internal standard. Bi was found to be satisfactory for this purpose and in order to assess the reproducibility of replicate arcings, a series of samples containing small amounts of In, Bi and Tl in constant proportions to each other and contained in the sodium chloride matrix were arced at 7 A. The spectral lines measured were: Tl 3775 Å, In 3256 Å and Bi 3067 Å. The samples were loaded into $^{3}/_{16}$" graphite electrodes the dimensions of the cavity being 3.2 mm (internal diam) $\times$ 5 mm (depth).

The replicate intensities of In, Tl and Bi and the intensity ratios of the line pairs In/Bi and Tl/Bi are shown in Fig. 1.

Standard deviations were calculated and were found to amount to 10.0% for the line pair In/Bi and 16.5% for Tl/Bi. The reproducibility for In can be considered spectrographically satisfactory, whereas that for Tl is only fair.

Extraction of the iodo-complexes of In and Tl into ethyl ether

As has already been stated, the extraction of the iodo-complexes of In and Tl into ethyl ether from a solution in which the hydriodic acid is generated *in situ* with the

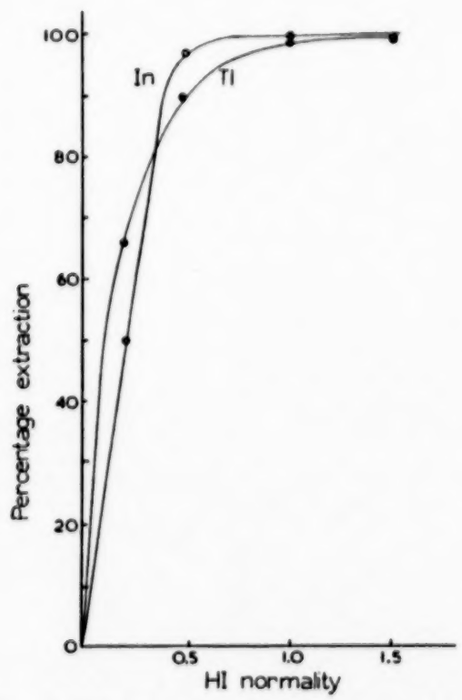

Fig. 2. The percentage extraction of the iodo-complexes of In and Tl as a function of HI normality.

aid of sulphuric acid is not satisfactory but hydrochloric acid is an excellent medium for the dissolution of silicate rock residues after removal of the silica with hydrofluoric acid. A series of experiments were therefore carried out to measure the percentage extraction of In and Tl from a solution of small amounts of these elements in 15% hydrochloric acid to which varying amounts of hydriodic acid were added. The hydriodic acid concentrations used were 0.2 *N*, 0.5 *N*, 1.0 *N*, and 1.5 *N*, respectively.

Sulphur dioxide was passed through each solution until the brown iodine colour had disappeared in order to ensure that all iodine was present in the anionic form and that the Tl was present completely in the monovalent state. Each solution was then shaken with an equal volume of ethyl ether which had been previously equilibrated with 15% hydrochloric acid. The aqueous and organic phases were then separated, taken to dryness and the residues collected in the sodium chloride matrix and the In and Tl determined spectrochemically using Bi as internal standard.

In Fig. 2 the percentage extraction figures are shown as a function of hydriodic acid normalities and it will be noted that the extraction of each element increases rapidly to a limiting value of about 99% at 1.0 *N* acid. This acid concentration was taken as the optimum for all future work bearing in mind the desirability of keeping all reagent concentrations down to a minimum.

Determination of In and Tl in silicate rocks

The method whereby the In and Tl concentrations were determined in 8 silicate rocks was as follows: 10-g samples of rock were digested in a 150-ml Teflon beaker with 50 ml of AR grade hydrofluoric acid and 50 ml of AR grade aqua regia[9]. The mixture was taken to dryness in a water bath and the residues were transferred to a borosilicate glass beaker to which 20 ml of sulphuric acid were added followed by heating until all the acid had been removed. The sulphated residues were then dissolved in the minimum quantity of 15% hydrochloric acid and the rock solutions divided into two equal volumes each representing 5 g of the original rock. Each duplicate had a final volume of about 200 ml. Sufficient AR grade hydriodic acid was now added to each solution to adjust the concentration of this acid to 1.0 *N*. Sulphur dioxide gas was then passed through each sample until the iodine colour had disappeared and the In and Tl were then extracted with an equal volume of pre-equilibrated ethyl ether in a 1000-ml separating funnel. Each ethereal extract was taken to dryness and a further 50 ml of 15% hydrochloric acid were added followed by the requisite amount of hydriodic acid. After treatment with SO_2, the trace elements were again extracted with an equal volume of the ether. The purpose of the double extraction was to effectively separate the In and Tl from other interfering elements in particular Fe and also to remove traces of sulphuric acid remaining from the sulphation stage of the procedure. If this acid is present, it is difficult to obtain a satisfactory dry and compact residue for packing into the electrodes due to "creeping" of the acid during the final stages of the technique.

The second ethereal residues were taken to dryness in 50-ml porcelain basins and the iodine removed by adding a few ml of nitric acid. The usual sodium chloride matrix and Bi standard were added in solution form and the residues were again taken to dryness. The samples were loaded into graphite electrodes and arced at 7 A in the wavelength range 2750 Å to 4680 Å.

Working curves were also prepared using amounts of In and Tl ranging from 0.02 to 2.0 μg in steps of 0.02, 0.04, 0.10, 0.20, 0.60 and 2.0 μg in 20 mg of NaCl. Each sample contained in addition 10 μg Bi as internal standard.

A further set of standards was prepared in which the In and Tl were in each case given a double extraction treatment exactly as the 8 silicate rocks. Both sets of standards when plotted on the working curve were indistinguishable from each other and indicated that the extraction procedure was completely effective.

RESULTS

A typical spectrogram (quartz felspar porphiry) is shown in Fig. 3 and it will be noted that the spectral lines are quite strong and clear. The experimental results are summarised in Table I and show gratifying agreement with independent data obtained on G-1 and W-1 by other workers using different experimental methods. The table also shows that good agreement has been obtained with the author's own previous work on anion exchange enrichment.

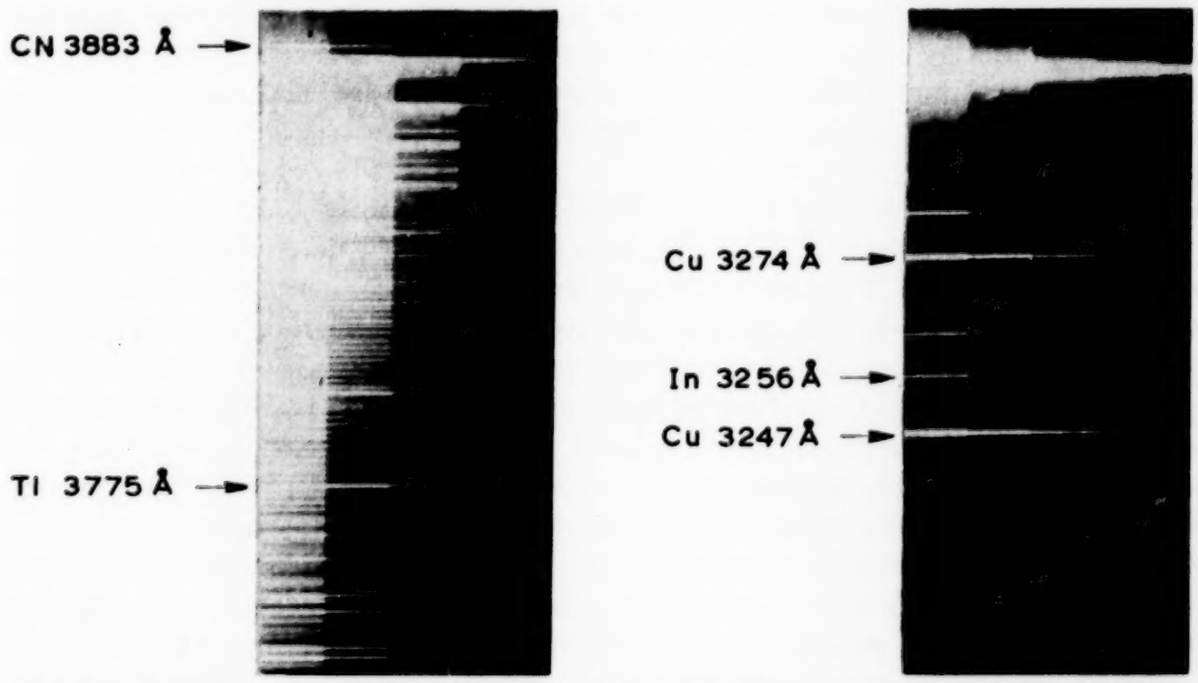

Fig. 3. Spectrogram of ether extract from solution of quartz felspar porphiry showing In and Tl lines.

TABLE I

THE ABUNDANCE OF Tl AND In IN SILICATE ROCKS (DATA FOR Mn ALSO INCLUDED)

Name of rock	*Locality*	*p.p.m. Tl*				*p.p.m. In*		*p.p.m. Mn*
G-1	Westerley, Rhode. I, U.S.A.	1.27[a]	1.30[b]	1.30[c]	1.27[d]	0.042[a]	0.026[e]	210[f]
Quartz felspar porphiry	Paresis igneous complex, S.W.A.	0.71[a]	—	—	—	0.070[a]	—	600[f]
W-1	Centerville, Virginia, U.S.A.	0.21[a]	0.17[b]	0.1[c]	0.11[d]	0.094[a]	0.064[e]	1300[f]
Gabbro	Paresis igneous complex, S.W.A.	0.18[a]	—	—	—	0.120[a]	—	1300[f]
Nepheline syenite	Paresis igneous complex, S.W.A.	0.59[a]	—	—	—	0.266[a]	—	1532[f]
Hortonolite dunite	Lydenburg, Tvl. South Africa	—	—	—	—	0.336[a]	—	5500[f]
Cape granite	Cape peninsula, South Africa	1.30[a]	—	1.40[c]	—	0.070[a]	—	—
Shale	Mouille point, Cape Town, S.A.	0.12[a]	—	0.18[c]	—	0.027[a]	—	—

[a] This paper
[b] MORRIS AND KILLICK[10]
[c] BROOKS, AHRENS AND TAYLOR[1]
[d] VINCENT[11]
[e] SMALES *et al.*[12]
[f] TAYLOR[13]

DISCUSSION

The agreement obtained for the abundance of Tl in G-1 is particularly striking and a figure of 1.29 p.p.m. is suggested with some confidence. Agreement for W-1 is not quite so good but the average of 0.15 p.p.m. for the four sets of data cannot be far from the truth. The author has obtained figures for the abundance of In in G-1 and W-1 which are about 50% higher than the figures obtained by SMALES *et al.*[12] by neutron activation, but considering that the two techniques are entirely different and that the concentrations concerned are particularly low, the measure of agreement is quite good. SHAW[14] has pointed out that there is no apparent regularity in the distribution of In in silicate rocks apart from a tendency to be associated with Sn. This has been noted by RANKAMA AND SAHAMA[15] and GOLDSCHMIDT[16] who have however suggested the possibility of an association with Mn since the respective ionic radii are extremely close (Mn^{+2} = 0.81 Å : In^{+3} = 0.80 Å). Fortunately, independent abundance data are available for Mn in 6 of the rock samples and an apparently fairly close association between the two elements has been noted in these samples. Fig. 4

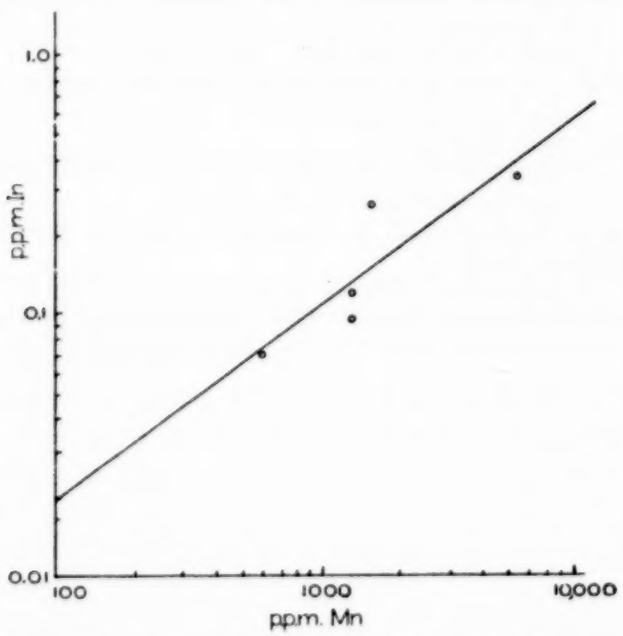

Fig. 4. In concentrations in six silicate rocks expressed as a function of Mn concentrations.

shows a log/log plot of In concentrations as a function of Mn concentrations. It is obvious that firm conclusions cannot be drawn from analyses on only six samples but there is no doubt that a further investigation into this apparent association would be of great interest and it should be possible to apply the method described in this paper to the speedy and efficient estimation of In and Tl in a large number of geological materials.

SUMMARY

A technique has been developed for the determination of In and Tl at very low concentrations in silicate rocks. The iodo-complexes of these elements are extracted from the rock silicate into ethyl ether and the ethereal residues are analysed spectrochemically. The optimum working conditions were established by a study of the variation of percentage extraction as a function of

hydrogen iodide normality; the reproducibility of the spectrochemical procedure was investigated. In and Tl were determined in eight silicate rocks including standard granite G-1 and standard diabase W-1. Good agreement was obtained with results of other workers for these two rocks and with the author's previous results. The evidence for a In/Mn coherence in silicate rocks is sufficiently strong to warrant further investigations.

RÉSUMÉ

Une méthode est proposée pour le dosage de très faibles quantités d'indium et de thallium dans des silicates. On procède à l'extraction des iodocomplexes de ces éléments, puis à leur dosage spectrochimique.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung sehr kleiner Mengen von Indium und Thallium in Silikaten durch Extraktion der Jodo-komplexe mit anschliessender spektrochemischer Bestimmung.

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CONTRIBUTIONS TO THE STUDY OF ORGANIC OSMIUM REAGENTS

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Investigations carried out by various workers on organic reagents for osmium indicate that this element mainly reacts with reagents containing the >C=S group. TSHUGAEFF[1] reported that osmium reacts very sensitively with thiourea. This reaction was used by SANDELL[2] for the detection of osmium in meteorites. The reactions of osmium with thiourea derivatives were studied by STEIGER[3] who examined 21 derivatives with the general formula $(R_2N)_2CS$. YOE AND OVERHOLSER[4] studied the reaction of 60 thiourea derivatives with 78 inorganic ions including osmium and ruthenium. BARDODĚJ[5] investigated a series of organic reagents and considered the >CS group as the functional analytical group for osmium and ruthenium.

Recent work[6] included an investigation of the colour reactions of osmium with two mono-substituted thiourea derivatives, namely: 4-acetylaminobenzaldehyde-thiosemicarbazone and 4-nitrobenzaldehyde-thiosemicarbazone, both reactions being more sensitive than the thiourea method.

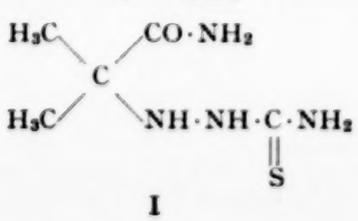
The present paper reports the reactions of osmium with two other mono-substituted thiourea derivatives and with four organic heterocyclic compounds containing the —SH group attached to the ring.

REAGENTS AND PROCEDURE

Reagents

Osmium tetroxide solutions were prepared by dissolving approximately 1 g of OsO_4 in 100 ml of 0.2 *M* sodium hydroxide, the titre of the solution being ascertained by the KLOBBIE method[7]. The osmium content of the test solutions was 49.12 μg Os/ml and 41.44 μg Os/ml, respectively.

The following reagents were used: I, The amide of α-thiosemicarbazido-isobutyric acid[8]; II, α-thiosemicarbazido-isobutyronitrile[8]; III, 3,5-dihydroxy-6-mercapto-1,2,4-triazine (disodium salt)[9]; IV, 3-mercapto-5-hydroxy-6-methyl-1,2,4-triazine[10]; V, 3-mercapto-5-hydroxy-6,6-dimethyl-1,6-dihydro-1,2,4-triazine[8]; VI, 2-mercapto-4-hydroxy-6-methyl-1,3-pyrimidine[11].



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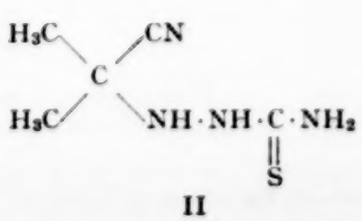

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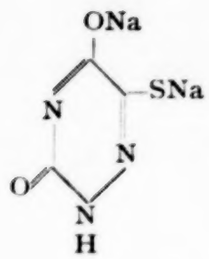

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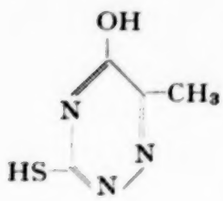

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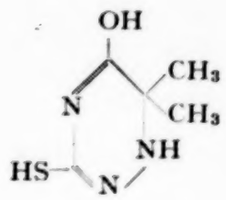

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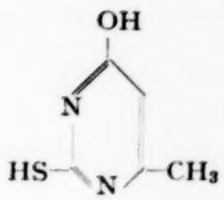

VI

Reagents I and II were used as 0.1% solutions in 1% sodium hydroxide. Reagent III was used as a 0.2% solution in water. Reagents IV, V and VI were used as 0.2% solutions in 1% sodium hydroxide. In each case 2 ml of reagent solution was added both to the test solution and to the blank.

Procedure

Pipette 0.25–6 ml of the osmium solutions in to 10-ml calibrated beakers. With reagents I, II, III, IV and VI, add 1 ml of sulphuric acid solution (32 ml of concentrated acid and 68 ml of water), while with reagent V, add 0.25 ml of the same acid solution. Then add the reagent solution and dilute to 10 ml with ethanol. With reagent I, a yellow colour is obtained which develops steadily, the reading being taken after 10 min. With reagent II, a yellow-brown colour is obtained, the reading being taken during the first 5 min. With reagent III, a red-brown colour is obtained, the reading being taken during the first 10 min since the extinction decreases steadily. With reagent IV, a yellow colour is obtained which develops steadily, the reading being taken after 20 min. With reagent V, a yellow colour is obtained, the reading being taken during the first 10 min since the extinction decreases steadily. With reagent VI, a pink shade is obtained.

Owing to the fact that reagent VI exhibits a low sensitivity, quantitative tests were carried out with the first five reagents only.

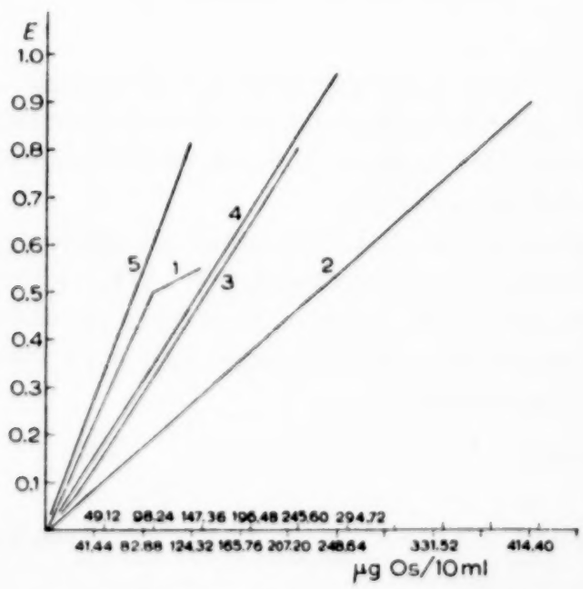

Fig. 1. Extinction curves. 1. I M-43; 2. II M-43; 3. III M-47; 4. IV M-50; 5. V M-43.

TABLE I

ml Os solution	*μg Os per 10 ml*	*Reagent I M-43*	*Reagent II M-43*	*Reagent III M-47*	*Reagent IV M-50*	*Reagent V M-43*	*Reagent VI M-43*
0.25	12.28	0.06	—	0.04	—	—	—
	10.36	—	—	—	0.04	0.07	—
0.5	24.56	0.125	—	0.08	—	—	—
	20.72	—	0.045	—	0.08	0.145	—
1.0	49.12	0.25	—	0.16	—	—	—
	41.44	—	0.09	—	0.16	0.29	—
2.0	98.24	0.50	—	0.32	—	—	—
	82.88	—	0.18	—	0.32	0.58	0.08
3.0	147.36	0.55	—	0.48	—	—	—
	124.32	—	0.27	—	0.48	0.81	—
4.0	196.48	—	—	0.64	—	—	—
	165.76	—	0.36	—	0.64	—	—
5.0	245.60	—	—	0.80	—	—	—
	207.20	—	0.45	—	0.80	—	—
6.0	294.72	—	—	—	—	—	—
	248.64	—	0.54	—	0.96	—	—
higher concentration	331.52	—	0.72	—	—	—	—
higher concentration	414.40	—	0.90	—	—	—	—

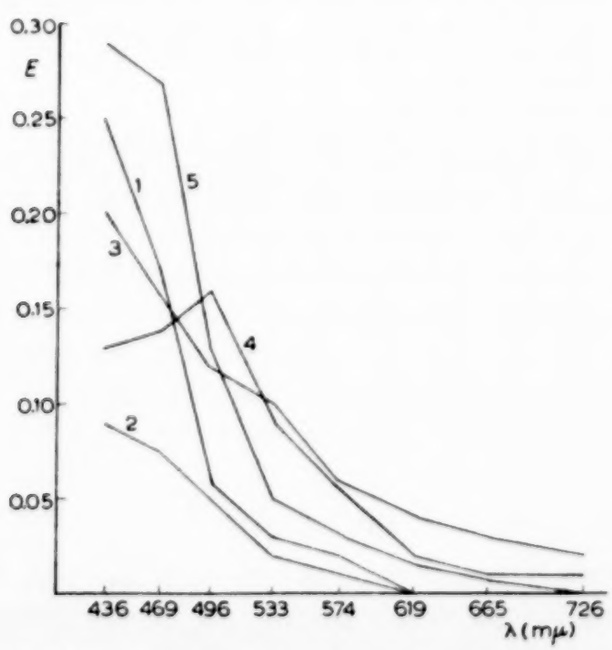

Fig. 2. Colour curves. 1. I-49.12 μg Os/10 ml; 2. II-41.44 μg Os/10 ml; 3. III-49.12 μg Os/10 ml; 4. IV-41.44 μg Os/10 ml; 5. V-41.44 μg Os/10 ml.

Readings were taken by means of a vertical Pulfrich photometer, the maximum extinction being obtained on the M-43 filters with reagents I, II, III, V and VI, and on the M-50 filter with reagent IV. The results are shown in Table I and in Figs. 1 and 2.

The results shown in Table I and Fig. 1 show that reagent I allows the determination of osmium in the range 1.23–9.82 μg Os/ml; reagent II, in the range 2.07–41.44 μg Os/ml; reagent III, in the range 1.23–24.56 μg Os/ml; reagent IV, in the range 1.04–24.86 μg Os/ml; reagent V, in the range 1.04–8.29 μg Os/ml.

These results, as well as the data mentioned in a recent paper[6], show that both from sensitivity and colour stability considerations, the reagents derived from thiourea are to be preferred to those containing a heterocyclic nucleus with the —SH group attached to the ring.

SUMMARY

The reaction of osmium is examined with two thiourea derivatives and four heterocyclic nitrogen compounds containing the SH-group attached to the ring, and five new colorimetric methods for the determination of osmium in the range 1.04–41.44 μg Os/ml are proposed.

RÉSUMÉ

Après avoir examiné le comportement de l'osmium avec deux dérivés de la thiourée et quatre composés hétérocycliques azotés renfermant un groupe SH, les auteurs proposent cinq nouvelles méthodes pour le dosage colorimétrique de cet élément.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Reaktion von Osmium mit Derivaten des Thioharnstoffs und mit N-heterocyclen, die eine SH-Gruppe tragen. Es werden 5 neue colorimetrische Bestimmungsmethoden für Osmium vorgeschlagen.

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THIONIN DERIVATIVES IN THE EXTRACTION AND DIRECT PHOTOMETRIC DETERMINATION OF BORON*

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Monomethylthionin and methylene blue (tetramethylthionin) have been thoroughly investigated by PÁSZTOR *et al.*[1,2] and DUCRET[3] and applied to the extraction and direct determination of boron. A detailed investigation has shown that other commercially available thionin derivatives can also be used advantageously for the same purpose. Thionin itself is not satisfactory but dimethylthionin (Azure A), trimethylthionin (Azure B), dimethyl-diethylthionin (New Methylene Blue N), mono-nitro-tetramethylthionin (Methylene Green), methyl-N-dimethylthionin (Toluidine Blue O) and the eosinates of Azure A and B were found suitable. In addition more than thirty solvents, mostly chlorinated or brominated hydrocarbons, were tried as extraction media. Using different dyes and solvent combinations various boron concentration ranges can be covered with good accuracy and reproducibility.

APPARATUS AND REAGENTS

Apparatus

For the spectrophotometric work a Beckman Model DU and a Cary recording spectrophotometer were used with 1-cm quartz cells. For the routine part of this work the Model B Beckman spectrophotometer was used. Except for storing and measuring the organic solvents polyethylene ware was used in all experimental work.

Reagents

Standard borofluoride (BF_4^-) solution containing 1.0 μg of boron per ml was prepared by dissolving reagent grade boric acid in 0.25% HF. This solution was used only after standing 24 h to insure complete formation of BF_4^-. 0.001-*M* aqueous dye solutions were prepared from commercially available (National Aniline) dyes. Reagent grade organic solvents were used for the extractions. Mixed solvents were prepared just before the extraction was carried out.

All reagents except the organic solvents were kept in polyethylene bottles and those containing hydrofluoric acid were kept below 5°. (No purification of reagents was carried out unless noted.)

PROCEDURE

10.0 ml of standard BF_4^- solution (containing 10 μg B) were diluted in a 100-ml polyethylene bottle with 30.0 ml of water or 0.5 *N* H_2SO_4. 10.0 ml of 0.001 *M* dye

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solution and then 25.0 ml of the organic solvent were added. The bottle was capped and shaken well for at least 1 min. After the layers separated completely the absorbance characteristics of the organic phase were investigated and subsequent quantitative measurements made at the absorbance maximum. Reagent blanks were run in parallel.

If the absorbance was too high the organic phase was diluted (1 : 5 or 1 : 25) with the solvent so that the final absorbance was always less than 1.2. Reagent blanks were treated the same way and their values subtracted from the total absorbance to give the net absorbance.

DISCUSSION

The structure of methylene blue, first used for the solvent extraction of boron by DUCRET[3], suggested that other thionin derivatives or thionin itself might also be applicable. The commercially available derivatives, therefore, were investigated.

Preliminary experiments, using dichloroethane, carried out as described in the procedure, showed visually that most of the dyes form an extractible complex with BF_4^-. These were, in decreasing order of visible difference, MB (Methylene Blue), AB (Azure B), NMB (New Methylene Blue N), AB-eos. (Azure B Eosinate), AA-eos. (Azure A Eosinate), MG (Methylene Green), AC (Azure C), AA (Azure A), and TBO (Toluidine Blue O). No visible difference was observed with T (Thionin). The structural formulas of these dyes can be seen in Fig. 1.

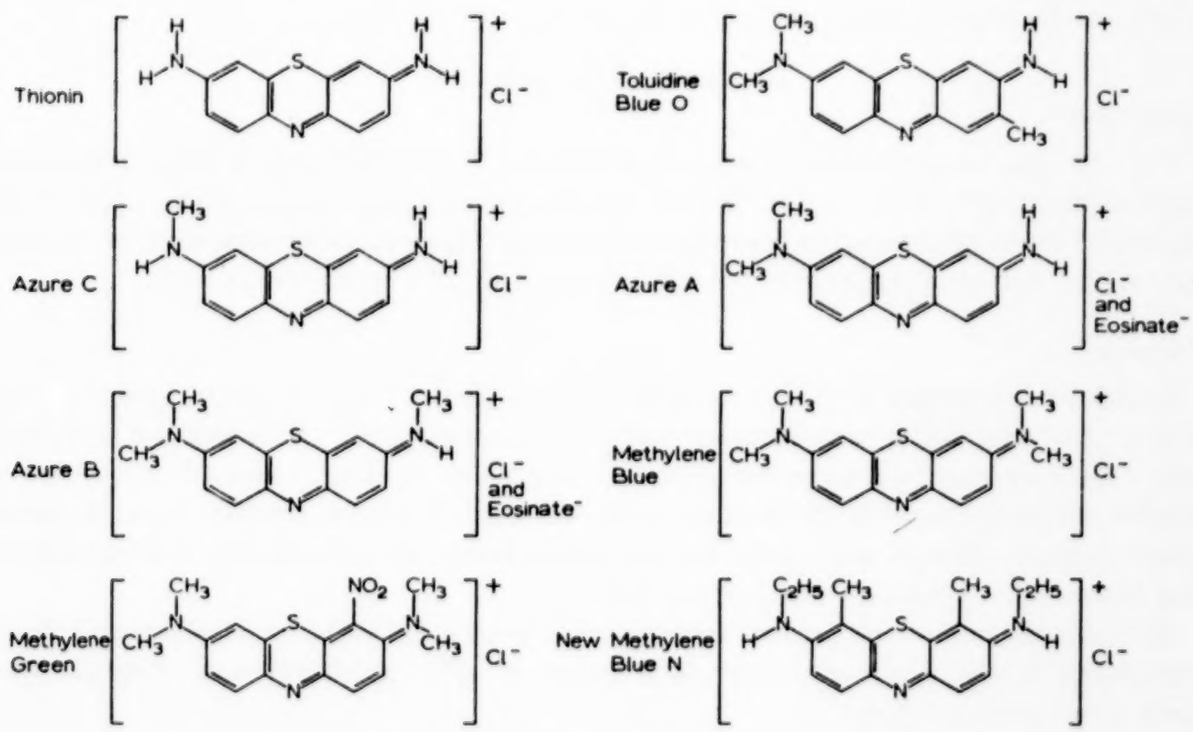

Fig. 1. Thionin derivatives tested.

Spectrophotometric measurements were carried out on solutions obtained by using the general procedure. It was observed that where a BF_4^-–dye complex was formed and extracted (with the exception of TBO and NMB), the absorbance maximum was

between 655–660 mμ (that of TBO was at 632 mμ and of NMB at 618 mμ) (Fig. 2). The absorbance maximums of the reagent blanks were approximately at the same wave lengths as their corresponding BF_4^-–dye complexes with the exception of TBO. These anomalous curves of TBO are shown in Fig. 2.

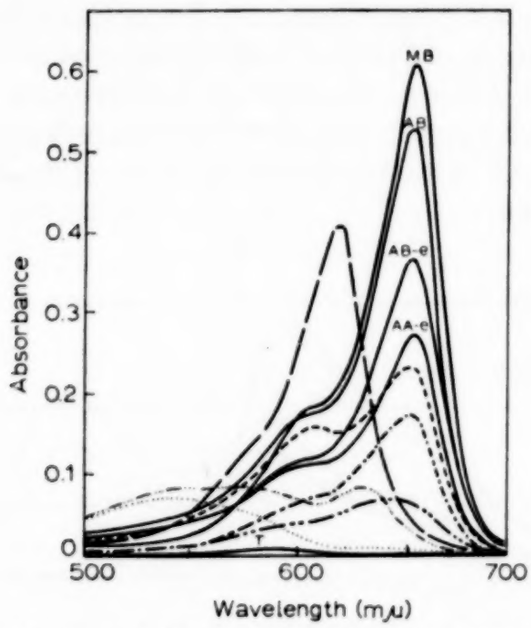

Fig. 2. Spectral absorbance curves of the extracted BF_3–dye complexes: ———— MB, AB, AB-e, AA-e, T; —— —— NMB; — — — — MG; - — - — - — AC; - - — - - — AA; ···—···— TBO; ..... TBO reagent blank.

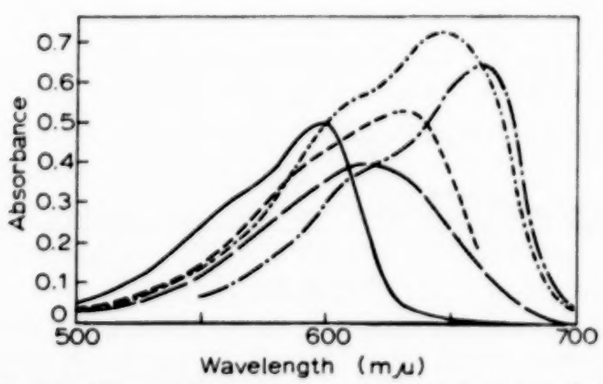

Fig. 3A. Spectral absorbance curves of 10^{-5} *M* aqueous dye solutions at pH = 3.0: ———— Thionin; —— —— —— Azure C; — — — — — — Azure A; - — - — - — - — Azure B; - —— - —— Methylene Blue.

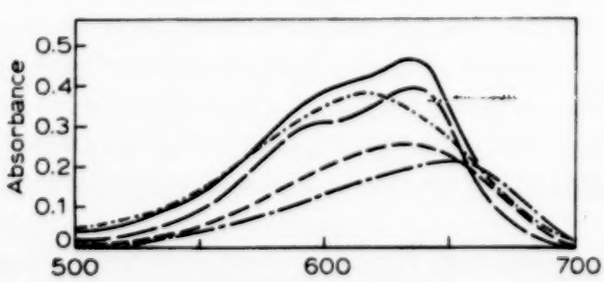

Fig. 3B. ———— Toluidine Blue O; —— —— —— New Methylene Blue; — — — — — — Azure A-eosinate; — - — - — - Azure B-eosinate; - — - — - — - — Methylene Green.

The absorbance maxima of these dyes in the original aqueous solutions varied from 614–663 mμ except for T at 597 mμ (Figs. 3 A and B).

Measurements with T showed a highest total absorbance value of less than 0.02 and a net absorbance less than 0.01 for 10 μg B. Net absorbances using the other dyes, again for 10 μg B, were of the following order (those greater than 1.2 are extrapolated values). MB 2.9, AB 2.0, NMB 1.9, AB-eos 1.6, AA-eos and MG 1.2, AC 1.0, AA and TBO 0.4. The reagent blank absorbance values decreased in the same order from 0.6 for MB to 0.08 for TBO. These results showed that by using different dyes with the same solvent (1,2-dichloroethane) various boron concentration ranges could be covered with good sensitivity without aliquoting, making most of the dyes attractive for analytical applications.

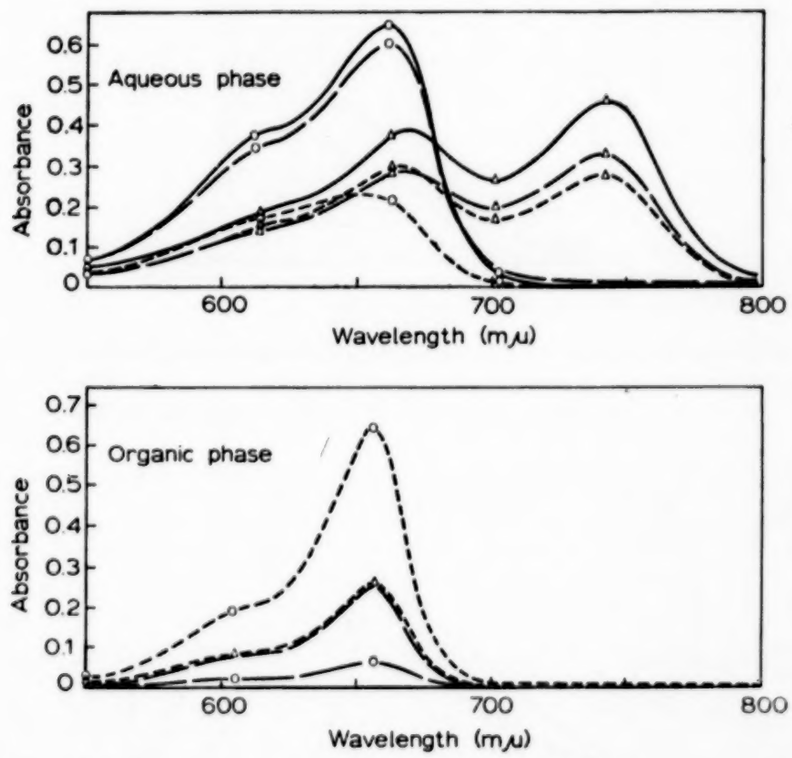

Fig. 4. Effect of pH and dichloroethane extraction on the absorbance curves of 10^{-5} *M* methylene blue solution. pH = 2.0: o————o before extraction; o— —o extracted–blank; o - - - - o extracted–10 μg B(as BF_4^-). pH = 0.0: Δ————Δ before extraction; Δ— —Δ extracted–blank; Δ- - - - -Δ extracted–10 μg B(as BF_4^-).

Figs. 4 and 5 show the effect of pH and extraction on both the aqueous and organic phases for Methylene Blue and Azure C with dichloroethane. The total and net absorbances do not change between pH 6 and 2 but decrease at lower pH levels[1,2]. The same trend was observed with other dyes. Correct results can be obtained between pH 2 and 0.25 by using higher dye concentrations and carefully controlling the acid concentration

To further improve the solvent extraction of boron with these thionin derivatives, various organic solvents were tried. Different solvent types were first checked including halogenated hydrocarbons, benzene, ethers and carbon disulfide. The BF_4^-–dye complexes behaved quite differently with the various solvents. Some did not extract

the complex at all but others, especially several of the chlorinated hydrocarbons (and to a lesser extent a brominated hydrocarbon) were universally suitable. Also the distribution of the colored boron complex between the aqueous and organic layers varied significantly.

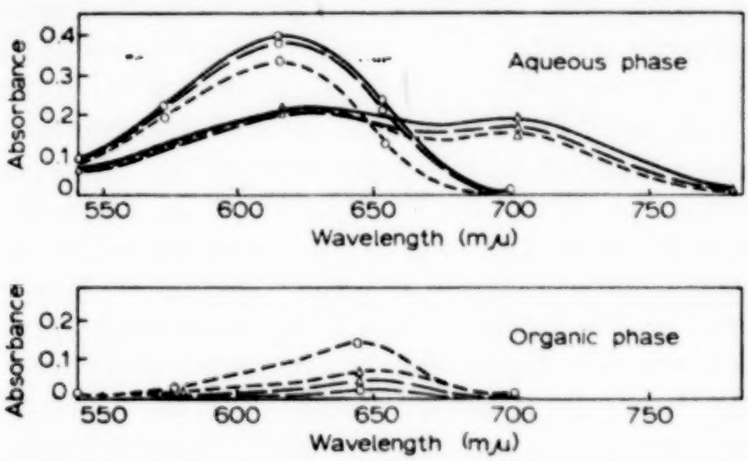

Fig. 5. Effect of pH and dichloroethane extraction on the absorbance curve of 10^{-5} *M* monomethyl thionin solution. pH = 2.0: o——o Before extraction; o— — —o extracted–blank; o— — — —o extracted–10 μg B(as BF_4^-). pH = 0.0: Δ— — —Δ before extraction; Δ——Δ extracted–blank; Δ— — — —Δ extracted–10 μg B (as BF_4^-).

No, or very limited, extraction was observed with benzene, 1,3-dimethylbenzene, diethylether, methylethylether, carbon disulfide, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, 2-chloropropane, 1-chlorobutane, chlorobenzene, *p*-dichlorobenzene in benzene, tetrachlorobenzene in benzene, hexachlorobenzene in benzene, hexachloroethane in benzene, bromoethane, 1,1,2,2,-tetrabromoethane and 1,2-dibromopropane. With all these solvents the total absorbance was less than 0.04 and the net absorbance less than 0.02 for 10 μg boron.

Carbon tetrachloride, chloroform and monochloroethane were found to be poor extracting solvents, the highest net absorbance values, those for MB, being respectively 0.02, 0.07 and 0.07. Monochloroethane, with a low boiling point, is also disadvantageous because the extraction must be carried out at around 6° or less.

Dichloromethane and *cis*-dichloroethylene behave similarly to 1,2-dichloroethane in that they give the highest net absorbances. Unfortunately the reagent blanks are relatively high for MB, AB, and NMB and 10 μg boron can be measured only after 1 : 5 dilution. With AB-eosinate, MG, AC, AA-eosinate, AA, and TBO, lower reagent blanks and satisfactory net absorbance values were obtained.

1,1,2-Trichloroethane and *o*-dichlorobenzene give lower absorbance values with correspondingly lower reagent blanks. *o*-Dichlorobenzene gives exceptionally low blanks with MB, and AB, making it an especially good solvent for use with these dyes. 1,2-Dichloropropane and 1,4-dichlorobutane extract the boron complexes even less but can be used for higher boron concentrations.

The dyes themselves are relatively soluble in 1,1,2,2,-tetrachloroethane and di-(β-chloroethyl)-ether making a 1 : 5 or 1 : 25 dilution of the extract necessary in order to read the absorbance. Although even with a 1 : 25 dilution measurable net absorbances were obtained, the high reagent blanks (80–95% of the total absorbance) make

these solvents unsatisfactory. These were the only solvents that extracted the T–BF_4^--complex appreciably, giving net absorbances of 0.25 and 0.36.

The brominated solvents with the exception of 1,2-dibromethane, which was a very poor extractant, proved completely unusable.

Solvent mixtures were also tried. Mixing a solvent into which the colored BF_4^--complex extracts readily with one which is a poor extractant makes adjustment of the sensitivity and range possible. An example of this is the use of 1,2-dichloroethane-1,2-dichloropropane (or carbon tetrachloride) mixtures with monomethylthionin as previously reported[2]. Many other variations are obviously possible.

The measurements reported in this paper were carried out according to the procedure using water as the diluent for the aqueous phase. When diluted sulfuric acid was used instead of the water, the same trends were observed but the net absorbance decreased with increasing acid concentrations[1,2]. Organic acids as well as nitric and, in higher concentrations, hydrochloric and hydrofluoric acids interfere.

Total and net absorbances depend not only on pH but also on the purity of the dye and of the solvent. Generally it can be stated that if the aqueous dye solution was purified by preliminary extraction with the solvent, reagent blanks were lowered by about 10%.

Organic acid impurities in the solvent will also cause high blank values and erroneous results. Extracting with 1 *N* aqueous NaOH and redistilling the solvent will eliminate these impurities. The commercial solvents used in our work did not contain enough impurities to warrant purification.

CONCLUSIONS

Thionin and nine of its derivatives form complexes with BF_4^- and, except for that of thionin itself, these can be used for solvent extraction and photometric determina-

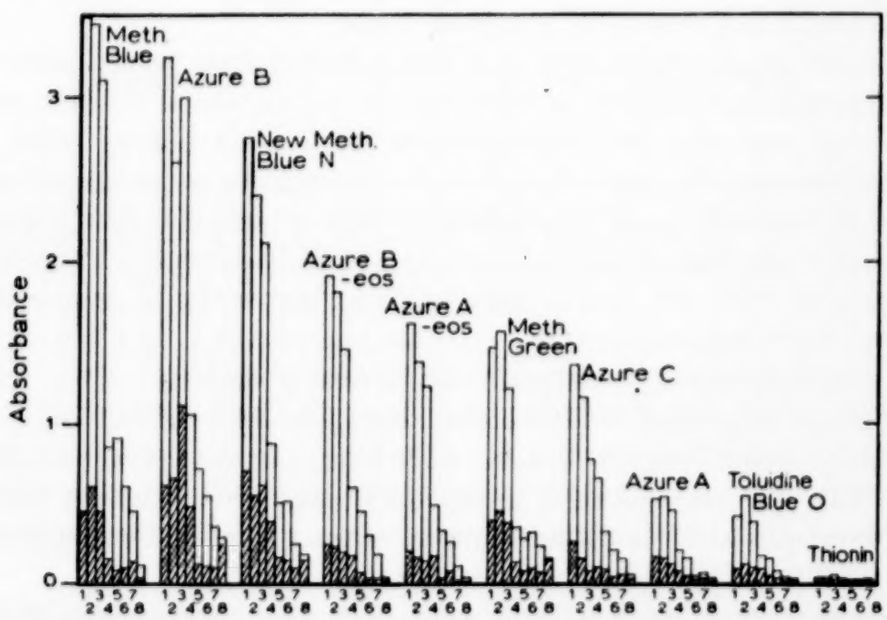

Fig. 6. Extractability of BF_3–thionin derivative complexes into different solvents. 1. *cis*-dichloroethylene; 2. 1,2-dichloroethane; 3. dichloromethane; 4. 1,1,2-trichloroethane; 5. *o*-dichlorobenzene; 6. 1,4-dichlorobutane; 7. 1,2-dichloropropane; 8. trichloromethane; □ net absorbance; // blank.

tion of boron. The complexes of the various dyes are extractible to different extents, but generally in the same order, in different solvents (Fig. 6) and solvent mixtures.

For analytical applications the following combinations can be recommended:

Dichloromethane 1,2-dichloroethane *cis*-dichloroethylene	AC, AA, AA-eos., TBO.
o-dichlorobenzene 1,1,2-trichloroethane	AC, AA-eos., AB, AB-eos., MB.
1,2-dichloropropane 1,4-dichlorobutane	AB and MB.

With solvent mixtures many other useful combinations are possible with all the thionin derivatives discussed here.

SUMMARY

Thionin and nine commercially available thionin derivatives were studied for their applicability in the analytical solvent extraction and direct photometric determination of boron. Azure A, Azure B, Azure C, Methylene Blue, New Methylene Blue N, Methylene Green, Toluidine Blue O, Thionin and the eosinates of Azure A and B were investigated. Over thirty organic solvents, mostly chlorinated or brominated were tried with these dyes. 1,2-Dichloroethane, 1,2-dichloropropane, dichloromethane, 1,1,2-trichloroethane, *cis*-dichloroethylene, *o*-dichlorobenzene, 1,4-dichlorobutane and mixtures of these solvents proved applicable. Many good dye–solvent combinations were found which were very attractive for the separation and determination of various amounts of boron. Only thionin itself proved unsatisfactory.

RÉSUMÉ

La thionine et neuf de ses dérivés ont été examinés en vue de leur utilisation pour l'extraction et le dosage photométrique du bore. Plusieurs solvants organiques ont été essayés. Seule la thionine n'a pas donné de résultats satisfaisants.

ZUSAMMENFASSUNG

Thionin und neun Derivate des Thionins wurden auf ihre Eignung zur photometrischen Bestimmung von Bor untersucht. Die zur Extraktion verwendbaren organischen Lösungsmittel werden angegeben. Thionin selbst ist nicht geeignet für die Bestimmung.

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DETERMINATION OF SULPHANILAMIDES WITH ALKYL NITRITES BY A POTENTIOMETRIC METHOD

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In the field of organic functional group analysis sulphanilamides have attracted special attention owing to their pharmaceutical importance. Several of the methods reported for the determination of sulphanilamides are based on acidimetric titrations of the amino group present in the molecule. Owing to the weak basic character of the amino group, the application of a non-aqueous titration and potentiometric end-point detection is necessary[1]. FRITZ AND KEEN[2] attempted the titration of the very weak acidic group $-SO_2NH-$ in non-aqueous media such as butylamine or dimethylformamide.

Certain recommended methods for aminosulphonamides depend on reactions of the amino group and such methods are mainly satisfactory. In general, acidimetric titrations are not specific for the sulphanilamides and hence reactions such as diazotisation[3] have been found more satisfactory (the method has been recognised as an official method)[4]; several workers have employed a diazotisation procedure with sodium nitrite as titrant and starch-iodide paper as external indicator or acriflavine[5] or diphenylbenzidine violet[6] as internal indicator; potentiometric end-point detection has also been applied.

Because of the limitations of sodium nitrite for quantitative diazotisation, MATHUR *et al.*[7] have recently employed alkyl nitrites for the determination of certain aromatic primary amines and compounds containing a reactive methylene group. Since alkyl nitrites were found to have advantages over sodium nitrite for quantitative diazotisation, the method has been extended to the determination of sulphanilamides.

EXPERIMENTAL

The procedure adopted for the preparation and standardisation of the alkyl nitrite solution was the same as described earlier[7]. Twice recrystallised sulphanilamide was used as primary standard as recommended by CALAMARI *et al.*[3]. The standard butyl nitrite solution was used to determine the amount of certain sulpha drugs in the commercial preparations. The titration was performed potentiometrically with a S.C.E. *vs.* a bright platinum indicator electrode, the equivalence point being indicated by a sudden change in the potential of the order of 80–120 mV. The sulpha drugs (tablets) employed in the present investigation were Sulphadiazine (Lederle), Sulphathiazole (Ciba), Sulphaguanidine (Ciba), Sulphapyridine (I.C.I.), Sulphamethazine (Ciba) and Sulphamerazine (Ciba). The graph (Fig. 1) represents a typical potentiometric titration curve of sulphadiazine and butyl nitrite. The sulpha drug contents

of the tablets given by the manufacturer and the values found experimentally are shown in the Table I.

In addition to the classical method, the "dead stop" technique with two platinum electrodes and a very small E (approximately 15 mV) was also used for end-point detection. The end-point is indicated by a sudden increase in the current due to depolarisation of the electrodes when a slight excess of nitrous acid is present.

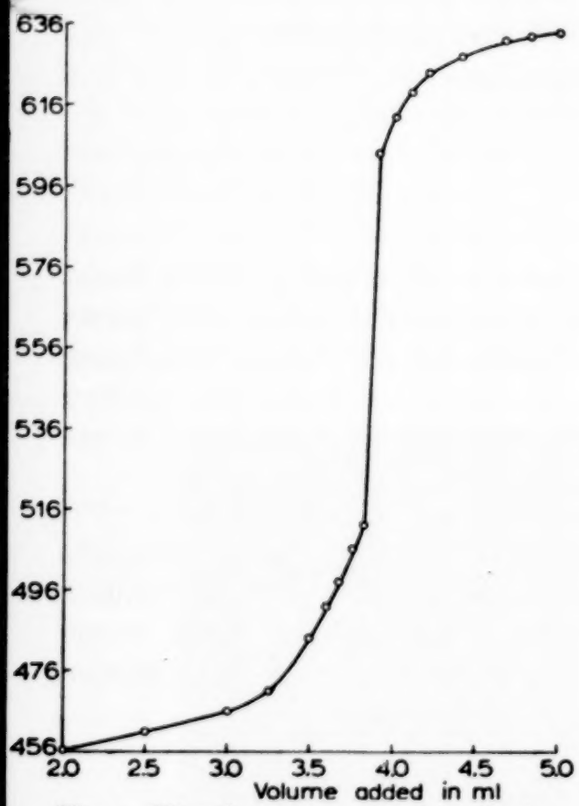

Fig. 1. Titration curve of sulphadiazine and butyl nitrite.

TABLE 1

Name of the sulpha drug	*Amount of sulpha drug per tablet*	
	Manufacturer's specification (g)	*Found (g)*
Sulphadiazine	0.5	0.487
Sulphathiazole	0.5	0.502
Sulphaguanidine	0.5	0.479
Sulphapyridine	0.5	0.484
Sulphamethazine	0.5	0.491
Sulphamerazine	0.5	0.478

ACKNOWLEDGEMENT

The authors are very grateful to PROF. K. P. HALDAR for his keen interest.

SUMMARY

A potentiometric titration with alkyl nitrite solutions is described for the determination of various sulpha drugs.

RÉSUMÉ

Une méthode est proposée pour le dosage potentiométrique de dérivés sulfamidés, au moyen de nitrite d'alcoyle.

ZUSAMMENFASSUNG

Beschreibung einer potentiometrischen Methode zur Bestimmung von Sulfamiden mit Hilfe von Alkylnitrit.

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OSZILLOPOLAROGRAPHISCHER NACHWEIS UND BESTIMMUNG VON JODAT UND PERJODAT

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(Eingegangen den 28. Oktober 1960)

In letzter Zeit untersuchten wir die Möglichkeit eines einfachen und schnellen Nachweises[1] und der Bestimmung[2] von Jodat neben Perjodat und umgekehrt. Dieses Problem ist wichtig nicht nur in der industriellen Praxis, wie z.B. bei der Erzeugung von Perjodsäure und bei der Reinheitskontrolle der bereiteten Präparate, sondern auch bei der Untersuchung der Oxydation von organischen Stoffen mit Perjodsäure und ihren Salzen.

Bei der oszillographischen Untersuchung (Verfolgung der Kurven $dV/dt = f(V)$) der angeführten Stoffe hat es sich gezeigt, dass es mit der oszillographischen Methode möglich sein wird nicht nur einen verlässlichen Nachweis durchzuführen, sondern auch beide Stoffe mikroquantitativ zu bestimmen. In der vorgelegten Arbeit wurde ausserdem eine Methode ausgearbeitet, die die Bestimmung auch von sehr kleinen Mengen Jodat in Perjodat und Perjodat in Jodat möglich macht.

EXPERIMENTELLER TEIL

Reagenzien

Kaliumjodat, Kaliumperjodat (KIO_4), Kaliumchlorid, Kaliumnitrat, Kaliumphosphat, Natriumperchlorat, Natriumazetat, Natriumsulfat, Kaliumkarbonat, Kaliumbikarbonat, Kaliumhydroxyd, Natriumhydroxyd, Chlorwasserstoffsäure, Schwefelsäure, Phosphorsäure, Oxalsäure, Essigsäure (p.a. Merck und Lachema). $(NH_4)_2H_3IO_6$, $K_4I_2O_9 \cdot 9\ H_2O$ und $NaIO_4 \cdot 3\ H_2O$ wurden laboratoriumsmässig hergestellt*.

Apparatur

Zur Verfolgung der Kurven der Funktion $dV/dt = f(V)$ wurden Elektronenröhren-Polaroskope Křižík P524 und P576 verwendet. Die Dauer des Quecksilbertropfens wurde mit einem mechanischem Tropfenabtrenner konstant gehalten.

Die Kurven wurden mit einem Fotoapparat Praktina aufgenommen, mit einem Flexon Objektiv mit Blende 1:2, mit Zwischenring, aus einer Entfernung von 25 cm auf Agfa Rapid Film. Die Expositionszeit war 1/25 oder 1/10 sec.

Als Vergleichselektrode wurde eine gesättigte Kalomelelektrode, der Quecksilberboden oder eine Graphitelektrode angewandt. Entsprechend der Konzentration der Ionen in der analysierten Lösung muss die Grösse des aufgezwungenen Stromes

* Wir danken Dr. M. DRÁTOVSKÝ vom Lehrstuhl für anorganische Chemie der Karlsuniversität in Prag, der uns diese Verbindungen zur Verfügung gestellt hat.

gewählt werden. Sie soll "so klein als möglich" sein, damit keine Störungen an der Quecksilbertropfelektrode entstehen.

ERGEBNISSE

Das oszillographische Verhalten von Jodat und Perjodat

Während in sauerem Medium (1 *M* HCl, 1 *M* H_2SO_4, 1 *M* H_3PO_4, 1 *M* Essigsäure und 1 *M* Oxalsäure) keine geeigneten Bedingungen für das Unterscheiden der beiden untersuchten Verbindungen gefunden wurden, wurde in neutralem, schwach alkalischem und alkalischem Medium gefunden, dass die Depolarisation von Perjodat und Jodat bei der Verfolgung der Kurven $dV/dt = f(V)$ sich durch klar ausgeprägte Einschnitte bemerkbar macht. In 1 *M* Lösungen von Natriumperchlorat, Natriumsulfat, Kaliumchlorid, Kaliumnitrat, Kaliumphosphat und Natriumazetat bildet Perjodat in dem kathodischen Teil der Kurve zwei Einschnitte, von denen der mehr positiv gelegene ($E = -0.1$ V S.C.E.) der Reduktion von Perjodat zu Jodat entspricht, und der zweite, der bei negativen Potenzialen auftritt ($E = -1.4$ V S.C.E.) der Reduktion von Jodat zu Jodid (Fig. 1). Die Reduktion von Jodat macht

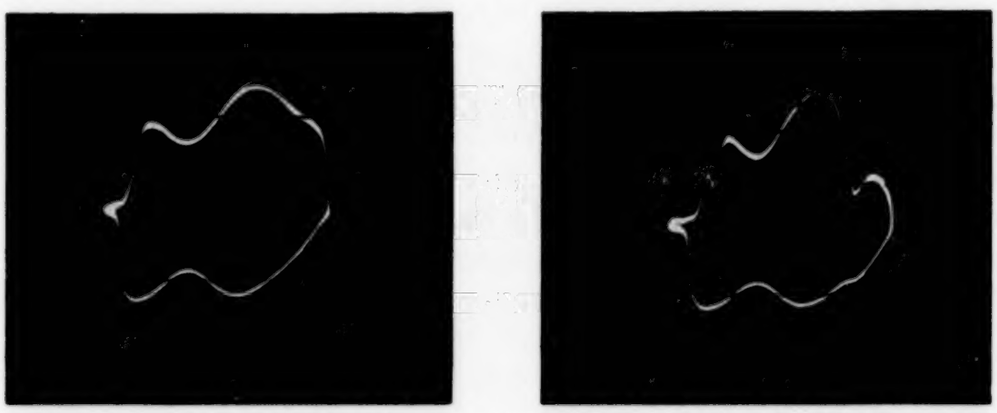

Fig. 1. Oszillogramme von Perjodat. (a) 5 ml 1 *M* KNO_3; (b) 5 ml 1 *M* KNO_3 + 0.15 ml 0.01 *M* KIO_4.

sich nur durch einen einzigen Einschnitt bemerkbar, dessen Depolarisationspotenzial ($E = -1.4$ V) dasselbe ist wie bei dem zweitem, mehr negativem Einschnitt des Perjodats; das wurde durch die Vertiefung und Vergrösserung dieses Einschnittes nach Zugabe von Jodat zu einer Perjodatlösung bewiesen. Um sicher zu sein, dass der kleinere, mehr positiv gelegene Einschnitt des Perjodats nicht durch eine eventuelle Verunreinigung des verwendeten Präparates verursacht wird, wurden dieselben Messungen auch mit Lösungen von $(NH_4)_2H_3IO_6$, $K_4I_2O_9 \cdot 9\ H_2O$ und $NaIO_4 \cdot 3\ H_2O$, die laboratoriumsmässig bereitet wurden, durchgeführt.

Da bekannt ist, dass die Redoxpotentiale beider Systeme durch den pH-Wert beeinflusst werden[3], wurde im weiteren das oszillographische Verhalten beider Verbindungen im Medium von Karbonatpuffern und alkalischen Hydroxyden untersucht.

In Lösungen von Karbonatpuffern von pH 8.4 bis 11.08 macht sich die Reduktion von Perjodat und Jodat auf diesselbe Weise bemerkbar, wie im Medium von neutralen Elektrolyten. Auf diese Weise ist es also nur möglich, Perjodat neben Jodat nachzuweisen. In allen Fällen ist es möglich, in 5 ml Elektrolyt 0.1 mg KIO_4 in Gegenwart

von grossen Jodatkonzentrationen nachzuweisen (Wechselstromkomponente: 0.2–0.6 mA — entsprechend der Jodatkonzentration — Empfindlichkeit 3–5, Quecksilbertropfelektrode-Bodenquecksilber).

In Kaliumhydroxydlösungen werden mit wachsender Konzentration im Bereich 0.2–5 *M* KOH beide Perjodateinschnitte weniger deutlich. Bei Hydroxydkonzentrationen höher als 2.5 *M* verschwindet praktisch der mehr negativ gelegene Einschnitt ($E = -1.4$ V), wobei an dem kathodischen Teile der Kurve bei mehr negativen Potentialen eine Deformation in Form einer länglichen Ausbuchtung auftritt. Das Jodat bildet aber unter denselben Bedingungen im ganzen untersuchten Konzentrationsbereich des Hydroxyds einen scharfen, ausgeprägten Einschnitt, dessen Potential sich praktisch nicht ändert ($E = -1.4$ V). Das kann zum Nachweis von Jodat neben Perjodat ausgenützt werden. In 5 ml 5 *M* KOH kann 0.1 mg KIO_3 verlässlich nachgewiesen werden. Bei Verwendung von Natriumhydroxyd als Elektrolyt (0.2–5 *M* NaOH) wurden praktisch dieselben Ergebnisse erzielt. Bei höheren Perjodatkonzentrationen entsteht zwar ein Niederschlag von Natriumperjodat, wodurch aber der Nachweis von Jodat nicht in grösserem Ausmasse beeinflusst wird.

Nachweis und Bestimmung von Perjodat in Jodat

Zum Nachweis und zur Bestimmung von Perjodat in Jodat kann als Elektrolyt direkt die wässerige Lösung der zu analysierenden Probe angewandt werden. Die Anwesenheit von Perjodat macht sich durch einen scharfen Einschnitt am kathodischen Teil der Kurve kenntlich, ($E = -0.1$ V S.C.E.), der derselbe ist wie der erste Einschnitt in anderen Lösungen neutraler Elektrolyte (Fig. 2).

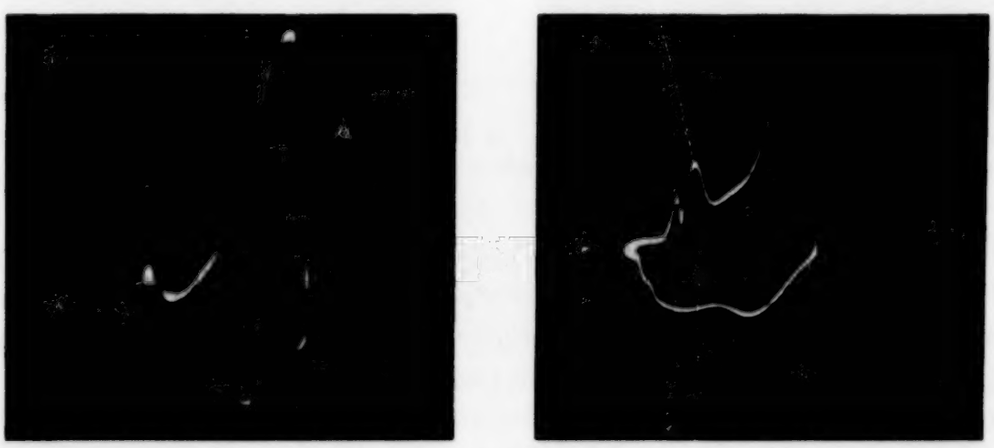

Fig. 2. Nachweis von Perjodat in Jodat. (a) 0.4 g KIO_3 in 5 ml H_2O; (b) 0.4 g KIO_3 + 0.46 mg KIO_4 in 5 ml H_2O.

Arbeitsgang. Eine Einwaage von 0.8 g KIO_3 wird in einem Messkolben von 10 ml Volumen in destilliertem Wasser gelöst und aufgefüllt. Nach volkommenem Durchmischen werden 5 ml in das elektrolytische Gefäss abpipettiert, und nach Einschalten des Gerätes wird die quantitative Auswertung entweder mittels der Methode der verschiebbaren Lichtachse, oder mittels der Methode der oszillographischen Komparationstitration[4] vorgenommen.

Aus dem Diagramm der Abhängigkeit der Einschnittiefe von der Perjodatkonzen-

tration (Fig. 3) geht hervor, dass optimale Ergebnisse unter den gegebenen Bedingungen dann erzielt werden, wenn die Konzentration des Perjodats im Jodat im Bereich von 0.05–0.17% liegt, d.h. dass eine Probe die mit einer höheren Perjodatkonzentration verunreinigt ist bei der Bereitung der Lösung mehr verdünnt werden muss, oder dass mit einer kleineren Einwaage gearbeitet werden muss.

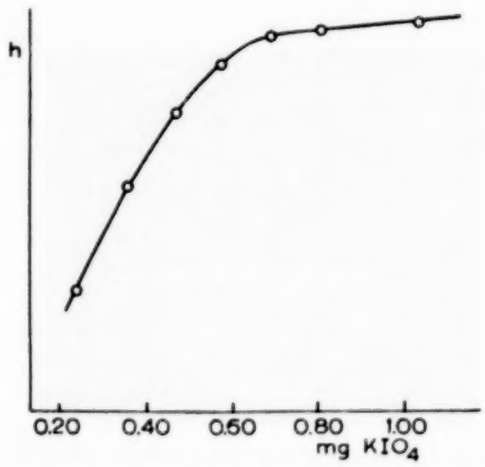

Fig. 3. Abhängigkeit der Tiefe des kathodischen Einschnitts des Perjodats von der Konzentration des KIO_4 in KIO_3 (0.4 g KIO_3 in 5 ml H_2O).

Der Fehler der Bestimmung bei Anwendung der Methode der verschiebbaren Achse, unter den angegebenen Bedingungen überschreitet nicht $\pm 10\%$ des Ergebnisses. Bei Anwendung der Methode der Komparationstitration wird als Vergleichselektrolyt ein reines Jodatpräparat, frei von Perjodatspuren, verwendet: in diesem Falle überschreitet der Fehler der Bestimmung nicht $\pm 5\%$ des Ergebnisses.

Nachweis und Bestimmung von Jodat in Perjodat

Für den Nachweis und die Bestimmung von Jodat in Perjodat wurde als der geeignetste Grundelektrolyt eine 5 *M* Natriumhydroxydlösung verwendet, in der Perjodat nur wenig löslich ist. Bei der Verwendung von Kaliumhydroxyd deformiert die hohe Perjodatkonzentration in der Lösung stark die Kurve der verfolgten Funktion. Der Potentialbereich ist dabei stark beschränkt, und auch bei Anwendung der höchsten Wechselstromstärken macht sich eine kleine Jodatkonzentration nicht durch einen Einschnitt bemerkbar. Kaliumhydroxyd wurde also nur zur Lösung der zu analysierenden Proben benutzt, durch Zugabe von Natriumhydroxyd wurde die Perjodatkonzentration durch Bildung eines Niederschlages so weit herabgesetzt, das der Jodateinschnitt gut kenntlich wurde und zu der Bestimmung verwendet werden konnte.

Arbeitsgang. Eine Einwaage von 1 g Kaliumperjodat wird in einem 10 ml Messkolben in 5 ml 5 *M* KOH gelöst, und nach volkommenem Durchmischen wird die Lösung schnell mit 10 *M* NaOH aufgefüllt. Nachdem wieder durchgemischt wurde, lässt man den Niederschlag absetzen, 5 ml der Lösung werden in das elektrolytische Gefäss genau abgemessen und nach Einschalten des Gerätes wird die quantitative Auswertung entweder mittels der Methode der verschiebbaren Lichtachse oder mittels der

Methode der oszillographischen Titration vorgenommen. Optimale Ergebnisse werden dann erzielt, wenn die Konzentration von Jodat im Perjodat im Bereich von 0.2–1% liegt.

Der Fehler der Bestimmung ist in diesem Falle etwas grösser, ±10–20% des Ergebnisses, denn der Jodateinschnitt wird durch eine hohe Perjodatkonzentration in der Lösung in gewissem Ausmasse beeinflusst (Fig. 4) und seine Messung ist schwieriger als im Falle der Bestimmung von Perjodat in Jodat.

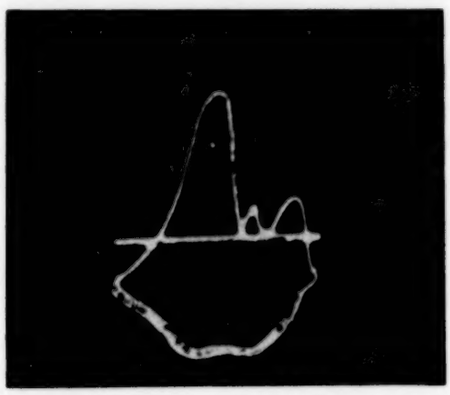

Fig. 4. Bestimmung des Jodats in Perjodat (0.8% KIO_3 in KIO_4).

ZUSAMMENFASSUNG

Es wurde das oszillopolarographische Verhalten von Perjodat und Jodat in saueren, neutralen und alkalischen Elektrolyten untersucht. Der Nachweis und die Bestimmung von Perjodat in Jodat kann unter Verwendung von Jodat als Elektrolyt vorgenommen werden, der Nachweis und die Bestimmung von Jodat in Perjodat unter Verwendung von 5 *M* Natriumhydroxyd als Elektrolyt.

SUMMARY

The oscillopolarographic behaviour of periodate and iodate has been investigated in acid, neutral and alkaline electrolytes. The detection and determination of periodate in iodate may be carried out using iodate as electrolyte and the detection and determination of iodate in periodate may be carried out using 5 *M* sodium hydroxide as electrolyte.

RÉSUMÉ

Les auteurs ont effectué une étude sur le comportement oscillopolarographique des periodate et iodate, dans divers milieux. Ils proposent des méthodes de dosage et d'identification pour ces deux anions, l'un en présence de l'autre.

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THE USE OF MICROCHEMICAL METHODS IN RADIOCHEMICAL ANALYSIS

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INTRODUCTION

The radiochemical analysis of a mixture of radioactive materials such as fission products normally involves the following essential series of operations:

(*a*) Addition to the sample of known amounts of carriers for the radioactive nuclides to be determined.

(*b*) Appropriate chemical treatment to ensure complete interchange between the inactive and active species.

(*c*) Chemical separation of the required elements from each other and any inactive materials present in the mixture.

(*d*) Rigorous radiochemical purification of each separated element to remove all traces of active impurities.

(*e*) Determination of the chemical yield of each carrier.

(*f*) Determination of the radioactivities of each recovered element by one or more appropriate counting techniques.

A useful alternative to the above involves the use of a radioactive tracer for the nuclide being determined instead of inactive carrier. The chemical yield is then determined by a suitable counting technique which distinguishes the added tracer from the nuclide being determined. This method is essential in the determination of isotopes of elements having no stable forms and may be of use in other cases. Examples are the use of ^{237}Np, which is an α-emitter, as a tracer for β-active ^{239}Np, and of ^{238}Pu as a tracer for ^{239}Pu. In the latter case the two α-emitters are determined by pulse analysis.

Perhaps the most widely known examples of radiochemical analytical procedures are those described by various authors and published in compilations edited by CORYELL AND SUGARMAN[1] and by MEINKE[2]. Since the issue of these publications numerous similar methods have been described and a number of laboratories have issued volumes of collected radiochemical procedures[3,4]. In most of these procedures, the weight of carrier element added is 10–20 mg and the chemical yield is determined gravimetrically, the final precipitate being collected and mounted in a form suitable for weighing and for counting. The whole of the recovered material is thus used for both purposes. The techniques used in the chemical separations and purifications are those of qualitative analysis using centrifugation instead of filtration; solution volumes are usually below 15 ml and rarely exceed 50 ml, most of the work being carried

out in centrifuge tubes of these two sizes. The weight of the final precipitate obtained is usually in the range 10–50 mg and is spread over an area of 2–10 cm^2, the latter varying from laboratory to laboratory and depending on the window size of the β-counter used. If the compound finally weighed is of stable and reproducible composition the accuracy of such a chemical yield determination is generally within the range 0.5 to 2.0%. This is considerably better than the accuracy of the β-activity determined by means of an end-window Geiger-Müller counter, the standard instrument most used for this purpose until a few years ago, and is comparable with that of β-counting with a gas flow proportional counter under ideal conditions.

Sources of error in absolute β-counting with end-window Geiger-Müller tubes have been discussed by a number of authors[5-8] and the general conclusions at that time (1950) was that after correcting for all possible errors the accuracy attainable was not better than about 5–10%. One of the main causes of error is that due to scattering or absorption of β-particles by the solid matter associated with the source. For a given amount of activity the effect of adding increasing amounts of inactive carrier is first to increase the observed counting rate and, with larger amounts of carrier, to decrease it, so that on plotting counting rate as ordinate against source weight as abscissa a curve is obtained rising to a maximum and then falling off approximately exponentially. The initial increase in counting rate is due to scattering of β-particles in the direction of the counter window by the solid carrier material and the subsequent fall occurs when self absorption becomes sufficiently great to outweigh the primary scattering effect.

The source thickness at which the maximum occurs varies widely with the maximum energy of the β-particles emitted. Consequently, the correction factors for a particular weight of carrier also vary widely with the β-particle energy. As an example the ruthenium isotopes ^{103}Ru (0.217 MeV) and ^{106}Ru (2.00 to 3.53 MeV from ^{106}Rh daughter) may be mentioned. The correction factors in a particular set-up for 20 mg/cm^2 of a ruthenium source containing these species were 2.06 and 0.78 respectively.

The accuracy of a radiochemical determination cannot be better than those of the correction factors, and experience showed that the accurate determination of these was a matter of some difficulty. In view of the variation and inaccuracy of such factors, therefore, it was decided that an effort should be made to reduce the weights of radioactive sources to a minimum. One way of doing this is to take sufficient of the original active sample so that a small aliquot of the separated and purified nuclide gives, on evaporation, a virtually weightless source. The chief disadvantage of this procedure is the large initial sample needed. The main bulk of each species separated must be used for the gravimetric chemical yield determination and the highly active dry precipitates so obtained could constitute undesirable sources of laboratory contamination and possible health hazard. In the case of samples of low activity this procedure is not possible as it is then necessary to count most of the recovered material.

From the above considerations it was decided that the best solution lay in the reduction to a minimum of the amounts of carrier used in radiochemical separations. We therefore investigated the feasibility of carrying out such separations using 0.5- to 1-mg amounts of carrier and it is the purpose of this paper to consider the problems that arise and to describe the experimental methods that we have used under these conditions.

EXPERIMENTAL

Separations on the 1-mg scale

Preliminary experiments were carried out involving the separation of the constituents of an inactive mixture of 1 mg of each of the elements, strontium, zirconium, molybdenum, silver, barium and cerium by conventional precipitation procedures.

Silver was first separated as chloride and cerium and zirconium hydroxides precipitated with ammonia. After the hydroxides had been dissolved in dilute nitric acid, cerous fluoride was precipitated by the addition of ammonium fluoride and zirconium recovered from the supernate by precipitation with ammonia after fuming with perchloric acid to remove hydrofluoric acid.

The ammoniacal solution of barium, strontium and molybdenum was treated with ammonium carbonate to precipitate barium and strontium. Molybdenum was then precipitated with α-benzoinoxime after acidification, and the barium and strontium separated by dissolving the carbonates in a little hydrochloric acid and precipitating barium chloride with a solution of 5 vols. concentrated hydrochloric acid and 1 vol. ether.

Each separated element was then subjected to an appropriate radiochemical purification process by the methods of HUME, GLENDENIN, BALLOU AND BOLDRIDGE[1]. Volumes of all solutions and quantities of reagents used were reduced to 1/10 or 1/20 of those specified in the original methods according to whether these employed 10 or 20 mg carrier.

No difficulties were experienced in these experiments which employed only precipitation reactions. Since then separations on the milligram scale have been carried out on a large number of elements, including most of the fission products, and we have found that ion-exchange and solvent extraction techniques, where applicable, to be particularly suitable at this level.

The techniques used with 1-mg quantities of carrier do not differ markedly from larger scale procedures. As solution volumes are 1/10 or less of those used for 10-mg amounts, most of the work can be done in 3-ml centrifuge tubes, though 10-ml tubes may be needed in the earlier stages of an analysis of a mixture of radio-nuclides and for the handling and efficient washing of bulky precipitates such as molybdenum α-benzoinoxime. We have found 10 × 75 mm test tubes to be very convenient and these are used in conjunction with a Eureka centrifuge. This is a simple and inexpensive centrifuge which takes two tubes and has the advantage of very rapidly reaching full speed form rest and *vice versa*. The speed is not very high but is adequate for most purposes. Where a high speed is necessary to separate a fine precipitate the Baird and Tatlock Angle Head Centrifuge is used. This takes 6 tubes and gives a maximum speed of 10,000 r.p.m.

Solvent extractions using about 1-ml volumes of solvent and aqueous phases may be carried out conveniently in 3-ml tubes. For extractions which proceed rapidly (*e.g.* uranium into ether, metal diethyldithiocarbamates into chloroform) sufficient agitation is given by the device known variously as a transfer pipette, fountain pen filler or "spitzer", *i.e.* a glass tube drawn out into a jet at one end and fitted with a rubber teat at the other. Slow extractions (*e.g.* complexes of thenoyl-trifluoracetone into benzene) are carried out in sealed polythene ampoules which are mechanically shaken[9]. Ion-exchange separations are generally carried out on columns 4–5 cm long and

4 mm in diameter, which are convenient for handling quantities varying between tracer and 1 mg as there is seldom more than a total of 4 mg of mixed carriers actually adsorbed on a column in one experiment. The most generally useful system involves Amberlite CG 400 anion resin and hydrochloric acid solutions, and a great deal of information about the behaviour of elements in this system is due to the work of KRAUS AND NELSON[10]. Such separations utilise large differences in distribution coefficients between elements and need only the simplest of apparatus.

Determination of chemical yield and source preparation

The feasibility of radiochemical separations and purifications with 1-mg amounts of carriers having been demonstrated the problem of determining chemical yields remained to be solved before it was possible to use the procedure for quantitative work. This problem had to be considered in relation to the method of source preparation.

When the work was started it was considered desirable to minimise back-scattering of β-particles by mounting sources on a light backing and for this purpose 0.0005 inch distrene foil, having a superficial density of 1.5 mg/cm^2 was used. This is stretched over a 1-inch diameter circular hole in a $3 \times 3^3/_8$ inch aluminium card and attached to the latter by adhesive. Sources are prepared by evaporation of known amounts of an aqueous solution of the radioactive material on the distrene, a small amount of insulin being used to spread the solution over a circle of about $\frac{1}{2}$ inch diameter. At a later stage β-counters were calibrated for various emitters by direct comparison with 4π gas and proportional counting and back scattering was no longer important. However, the above method of source preparation was found to be so convenient and the resulting sources proved to be so rugged that the procedure has been continued and is still in use.

Out of an initial 1-mg carrier added, up to about 0.5 mg may be present on the active source finally prepared. Even at this level the effect of solid source material on the β-count rate cannot be neglected and it is therefore still necessary to determine correction factors over a range of source weight for each nuclide counted. For weights between 0.5 mg and zero these factors are usually between 0.9 and 1.0; if sufficient activity is available sources containing less than 100 μg carrier may be prepared and here correction factors are very nearly unity. It is evident that the classical method of counting and determining the chemical yield gravimetrically on the same precipitate is not possible under these conditions. Counting and chemical yield determinations must, therefore, be carried out on different portions of the purified material. If the separated activity is low it may be necessary to count as much of the sample as possible. This only leaves, at the most, about 200 μg of carrier for chemical yield determination and it is therefore desirable that the chemical yield methods should be sufficiently sensitive to determine a few tens of micrograms of each element with an accuracy of 1 or 2%. The procedures should be quick and simple to carry out so that it is possible to do replicate determinations with the minimum of time and trouble.

The above requirements have been met by spectrophotometric and micro-titration procedures, the latter employing spectrophotometric end-point detection. It is, of course, desirable that the method used for a chemical yield determination should be specific for the element concerned. This is not always possible, however, and then it becomes necessary to use the same method for a number of different elements. In such case one must rely heavily on the radiochemical purification process to remove inter-

fering elements. This is generally adequate for the purpose but, if not, it may be necessary to introduce a step designed to remove a specific contaminant which may have been present in the original sample or introduced in the course of the radiochemistry. The possibility of impurities in the reagents used must also not be overlooked.

After purification of an element the material is finally obtained in solution, the total volume of which is adjusted to between 0.1 and 6 ml according to the total activity present. Occasionally it may be necessary to prepare a dilution if the activity is sufficiently high. Originally, portions for counting and chemical yield were measured by micro-pipette but it was soon found that the use of a weight burette in conjunction with a damped, weight-loading balance afforded a rapid, accurate and much more flexible method of dispensing solutions. The most convenient vessel for use as a weight burette has been found to be a blown polythene ampoule[9] with the neck drawn out into a capillary jet. The weight is about 2 g and the volume held about 6 ml. Filling and emptying are easily effected by squeezing and very fine control of delivery of drops is possible. The contents may be stored without loss by evaporation if the end of the jet is closed by means of a pair of tweezers whose tips have been heated for a few moments in a flame.

The same type of vessel is used for storing carrier solutions which are also dispensed by weight. These are prepared at a concentration of 10 mg of element per g of solution and from each an accurate dilution containing 200 μg per g is prepared. The dilute solution is stored in a sealed 50-ml polythene ampoule and portions are weighed out for standardisation at the same time as chemical yield samples.

Chemical yield determinations involve purely relative measurements and absolute standardisation of carrier solutions is not, therefore, necessary. The weight of carrier on the source may be required for determining the counting correction factor due to finite source weight but as this only needs to be known to about 10%, it would be sufficient to prepare the carrier solution to this accuracy. In spite of this we consider it desirable that carrier concentrations should be known to at least 1%, as this enables a constant check to be maintained on the functioning of the methods. Consequently, wherever possible, carrier solutions are prepared accurately by weight from suitable standard compounds having compositions known to be within 1% of theoretical. In other cases (*e.g.* ziconium) the carrier solutions are standardised by a suitable gravimetric method.

Spectrophotometric methods

The accuracy of a spectrophotometric procedure depends on the absorbancy of the solution being analysed and it may be shown[11] that, if Beer's Law is obeyed, it is a maximum at an absorbancy of 0.434 and varies only slightly between 0.2 and 0.7. This calculation is based entirely on the relation between absorbancy and the deflection of the null indicating instrument of the spectrophotometer. To minimise blank errors we prefer to keep absorbancy readings high rather than low and aim at values between 0.4 and 0.7. In designing a chemical yield method, therefore, the final volume of coloured solution and the cell length are chosen to give absorbancies in this range with a few tens of micrograms of element.

The instrument used for most measurements in a Unicam SP600, a glass prism spectrophotometer operating between 360 and 1000 mμ. The 4-cm cell needs a minimum of 8 ml solution and the largest volumetric flask which need be used, therefore, is a 10-ml.

A list of spectrophotometric methods which have been found suitable for chemical yield determinations is given in Table I together with other relevant information and references.

TABLE I

SPECTROPHOTOMETRIC METHODS

Element	*Method*	*Solution volume (ml)*	*Cell length (cm)*	*μg Element for absorbancy of 0.5*	*Wave length (mμ)*	*References*
P	Molybdenum blue	25	1	38	830	16
V	Phosphotungstic acid	10	4	34	400	16
Mn	Periodic acid	10	2	57	525	17
Fe	Thioglycollic acid	25	4	37	550	16
Co	Thiocyanate	10	4	45	620	16, 18
Ni	Dimethylglyoxime	25	2	36	450	16
Ge	Molybdenum blue	25	4	36	830	16
As	Molybdenum blue	25	1	38	830	16
Y	Bromopyrogallol red	25	1	23	660	19
Zr	Quercetin	25	1	42	440	20
Mo	Thioglycollic acid	25	4	56	365	21
Ru	Dithio-oxamide	25	4	36	650	16
Rh	Stannous chloride	10	4	42	480	16
Sn	Morin	20	2	56	430	22
Sb	Iodide	10	4	50	425	16, 23
Ce	Bromopyrogallol red	25	1	31	680	19
Rare earths	Bromopyrogallol red	25	1	36	660	19
Au	Hydrobromic acid	10	4	63	380	16
Bi	Iodide	25	4	30	460	16

Micro-titration methods

In titrations at the microgram level the indicator blank is a substantial fraction of the total titration and judgement of the end-point is difficult. Consequently instrumental procedures must be used, and we have employed potentiometric and spectrophotometric end-point detection. Micro-burettes of the micrometer syringe type are convenient and accurate and we have generally used the "Agla", made by Burroughs Wellcome Ltd. A maximum volume of 0.5 ml of solution may be delivered and the accuracy of rading is 0.0002 ml. In use, the glass jets supplied by the makers are replaced by home-made polythene ones which have the advantages of not being wetted by aqueous solutions and of being unbreakable.

A potentiometric end-point is employed in the determination of silver by titration with 0.002 *M* potassium iodide and of iodine as iodide by titration with 0.002 *M* silver nitrate. The bimetallic electrode system of CLARK[12] is used, consisting of two silver wires, one of which is amalgamated. The potential change at the end-point is

due mainly to the sluggishness of the response of the amalgamated electrode to changes in silver ion concentration. The titration is carried out in 2–3 ml of 0.1–0.2 *M* nitric acid solution which is contained in a 5-ml tall form beaker and stirred magnetically.

The Schwarzenbach method, adapted for spectrophotometric operation, is used for the determination of calcium, strontium, zinc, cadmium, barium and lead, the element being titrated with 0.0025 *M* disodium dihydrogen ethylene-diaminetetracetate (EDTA) using Solochrome Black W.D.F.A. (Eriochrome Black-T) as indicator. The titration is carried out in about 7 ml of ammoniacal solution in the presence of magnesium–EDTA complex to ensure an adequate colour change in the titration of barium and strontium which give only weak complexes with the indicator. In the titration of lead a little ammonium tartrate is added to prevent hydroxide precipitation.

The wave length used is 550 mμ, at which the absorption by the metal indicator complex is a maximum. The initial absorbancy, when all the indicator is combined with metal, is measured and the solution titrated to an absorbancy of 0.75 times this value. At the end-point half of the indicator is combined with metal and half is uncomplexed. If no volume change occurs the ratio of the initial to end-point absorbancy has been found to be 0.78, and the factor 0.75 includes a correction for the volume change during titration.

The titration unit, designed to fit into the cell carriage compartment of the SP600 is shown in Figs. 1, 2 and 3. It is constructed mainly of $^1/_8$-inch perspex sheet, blackened on the top surfaces to exclude stray light from the interior of the instrument, and consists of two main parts A and B, with a perspex cell C which has a light path of 2 cm and is 3 cm high and 1.8 cm wide.

Part A, the upper assembly, carries the cell and Agla burette. The end of the plunger and face of the micrometer are held in contact by the tension of a thread fastened

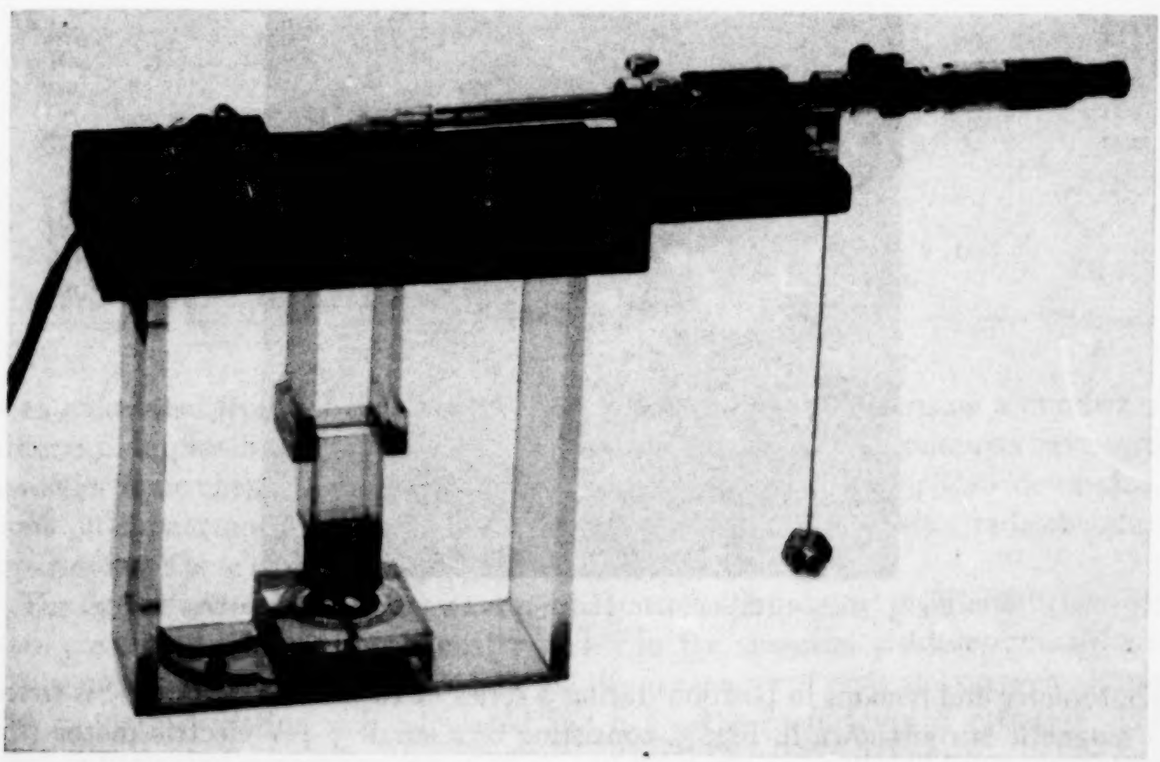

Fig. 1. Micro-titration unit assembled for use.

at one end to a collar holding the plunger and which passes over a cylindrical nut and supports a weight hanging at the other end. The cell C has flanges along two of its upper edges which slide into grooves provided in the holder attached to the bottom of A. Part B, the lower assembly, fits into the cell carriage compartment of the spectro-

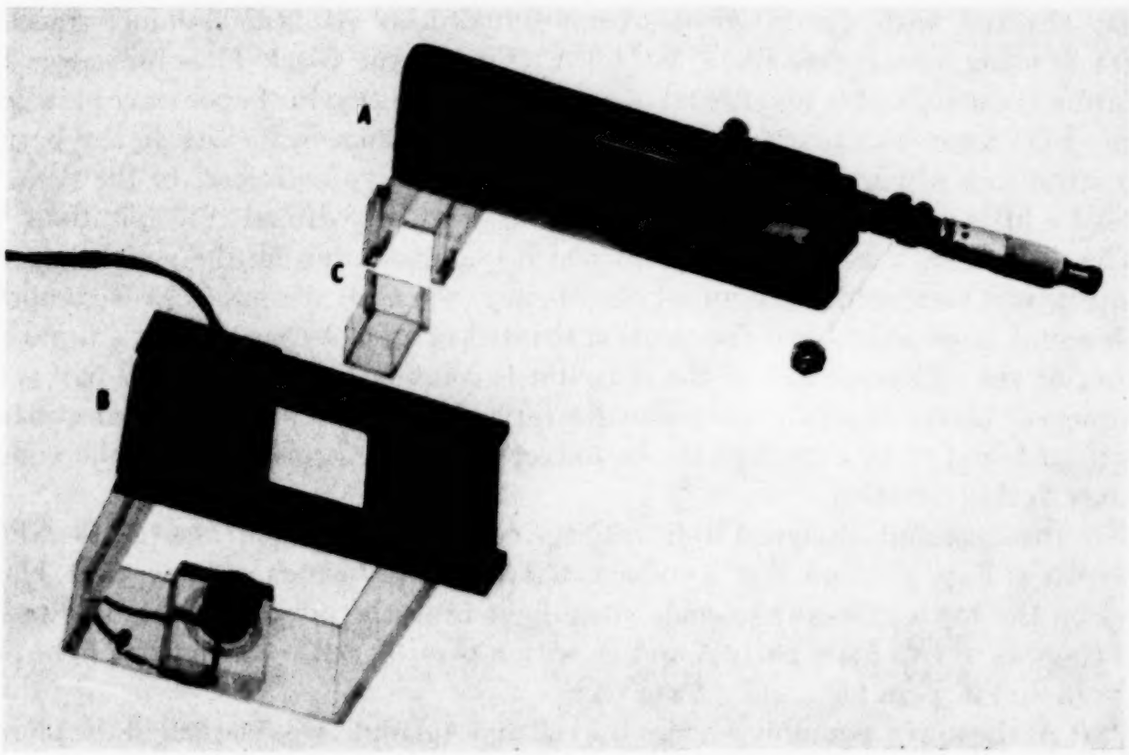

Fig. 2. Micro-titration unit showing the component parts A, B and C.

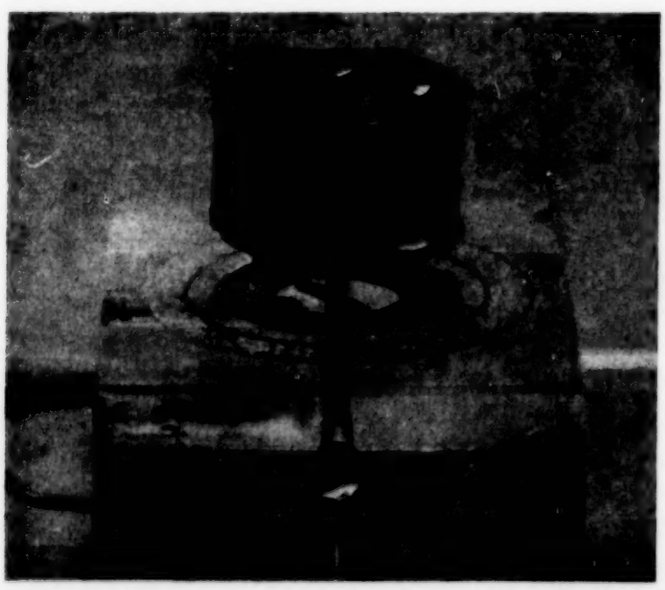

Fig. 3. Micro-titration unit. Enlarged view of magnetic stirrer.

photometer and remains in position during a series of titrations. In its base is fitted a magnetic stirrer shown in Fig. 3, consisting of a small 3–4 V electric motor (the "Electrotor" Type 240 is suitable) which is mounted upside down and held by its

spindle. A piece of phosphor bronze strip is soldered to one of the two motor contacts and brushes the surface of a brass ring set into a perspex block which also holds the spindle. The other contact is made via the grub screw holding the spindle in the perspex block, the spindle itself and a strip of brass soldered to the top of the motor and in rubbing contact with the top of the spindle. Also attached to B are the switch and variable speed control resistance which are connected in series with a 3-V battery and the motor via the brass ring and spindle. When the current is switched on the motor body rotates around the spindle, and rotation of the field magnet drives the stirrer, which consists of a short piece of steel wire sealed in polythene, at the bottom of the cell.

When the unit is in position inside the SP600 the light beam passes centrally through the cell, the bottom of the beam being well clear of the rotating stirrer and burette jet.

Accuracy of radiochemical procedures and chemical yield methods

The coefficients of variation of radiochemical procedures for determining ^{99}Mo, ^{111}Ag, ^{115}Cd and ^{140}Ba using 0.5 to 1 mg of carrier are given in Table II. These have

TABLE II

COEFFICIENTS OF VARIATION OF CHEMICAL YIELD METHODS AND OF COMPLETE RADIOCHEMICAL PROCEDURES

Element	*Chemical yield procedure*			*Nuclide*	*Complete radiochemical procedure*		
	μ	k	Σn_i		μ	k	Σn_i
Co	1.2	22	56				
Ni	1.2	33	67				
Sr	1.1	61	134				
Y	1.2	48	103				
Zr	1.2	39	97				
Mo	1.0	56	119	^{99}Mo	3.6	36	221
Ru	1.1	34	80				
Ag	0.8	51	114	^{111}Ag	3.4	22	101
Cd	1.0	67	143	^{115}Cd	5.1	32	164
Ba	1.0	71	146	^{140}Ba	5.6	34	172
Ce	1.0	61	139				
Rare earths (Pr, Nd, Sm, Eu, Gd, Tb)	1.0	64	133				

been calculated from the results of 2 to 11 replicate determinations on a number of different samples of solutions of mixed fission products. Similar calculations have been made for some chemical yield methods using the results of 2 to 4 replicate determinations on carrier and on the purified active solutions obtained after radiochemical separations. These results are also given in Table II.

The figures are realistic and were obtained in routine analyses; 18 different chemists were concerned in the radiochemistry and 9 in the chemical yield determinations.

The method of calculation was a follows: From each set of replicates on each sample the standard deviation was calculated and hence the coefficients of variation. The normal method of calculation was used for 4 or more observations but when only 2 or 3

results were available the method of small number statistics[13] was used. This involves multiplying the range by 0.89 or 0.59 for 2 or 3 results respectively to give the standard deviation, and gives a rather higher figure than the normal method.

If μ_i ($i = 1$ to k) are the individual values of the coefficient of variation, each being calculated from n_i observations, then the best value of the coefficient of variation μ is given by[14]

$$\mu = \sqrt{\frac{\Sigma n_i \mu_i^2}{\Sigma n_i}}$$

where Σ signifies summation between the limits of $i = 1$ and $i = k$. k is the number of different samples examined and Σn_i the total number of determinations made. μ is the coefficient of variation of a single determination.

The chemical yield determination involves replicate determinations of the concentrations of two solutions, the carrier and the final active solution, and a calculation involving the ratio of the two concentrations. Using the normal formulae for determining the standard deviation of arithmetically combined quantities it is readily shown that the coefficient of variation of a chemical yield is about equal to μ when the determination of each concentration is carried out in duplicate, and less than μ when more replicates are done. In general, therefore, we should not expect the coefficient of variation of a chemical yield to be worse than the values given in Table II.

The radiochemical procedures used were those of GLENDENIN AND BALLOU[1], and most of the measurement of β-activity were made with gas flow proportional counters of either 4 π or end-window type, a 9:1 mixture of argon and methane being used as counting gas. Some results from Geiger-Müller counters are also included. Under our conditions of use, in which frequent checks were made with long lived standard sources (^{204}Tl) and appropriate corrections made for counter variation, no significant difference in accuracy between the Geiger-Müller and the more stable proportional counters was observable.

The results for the radiochemical determinations of ^{99}Mo, ^{111}Ag, ^{115}Cd and ^{140}Ba show that the contributions made to the overall errors by the chemical yield procedures are insignificant. We attribute the major source of error to β-counting. Recent results[15] of careful intercomparison of 4 π β-counting techniques between various laboratories in the U.K., Canada and U.S.A. gave coefficients of variation of up to 3%. This work was carried out with virtually carrier free sources of ^{60}Co, ^{22}Na and ^{90}Sr–^{90}Y and we would expect a greater variation than this under our routine conditions with rather thicker sources.

DISCUSSION

The micro-techniques for radiochemical analysis described above have been in routine use in this Establishment since 1954. The reasons for their adoption have been dealt with in the Introduction but in use other advantages quickly became apparent. These are:

(*a*) Reduction in space and volumes of reagents needed. This is of particular value in utilising space in active fume cupboards which never seem to be large enough for radiochemical work.

(*b*) Elegance and speed. The use of small volumes of solution saves time, particularly in evaporation.

(*c*) Flexibility and replication. By weighing out portions of the final solution optimum amounts for counting and chemical yield may be obtained. Also, errors may be minimised by replication of chemical yield determinations and preparation and counting of sources.

(*d*) Adequate accuracy of chemical yield determination even when the yield is very low, as occasionally happens. In the worst cases all the material may be counted and the chemical yield determined on the source when this is finished with.

(*e*) If α-emitters are to be determined on the same sample it is of advantage to have the minimum total solid material present to ensure the production of as thin α-sources as possible.

Difficulties could arise in the application of these techniques in exceptional circumstances. The only case we have experienced has been in the determination of active strontium isotopes in occasional samples containing much calcium, when the radiochemical procedure has not been quite adequate to remove all the calcium, giving erroneously high chemical yields. This can be overcome by modifying the procedure, but the radiochemical analysis of any samples containing much solid material should be carefully considered to ensure adequate chemical as well as radiochemical purification. The possibility of the presence in the sample of the stable forms of radio-nuclides being determined should be borne in mind also, as erroneous chemical yields could result. In such cases chemical determinations of the elements in question must precede radiochemical analysis.

The further reduction of carrier weight by a factor of 10 would allow the virtual elimination of source weight corrections in β-counting in all but the very softest of emitters. At the 100-μg level precipitation reactions become less useful as it is not practicable to reduce solution volumes below the present minimum of 1–2 ml and hence solubility begins to limit the chemical yields attainable. One way out of this difficulty has been described by RUDSTAM[24] who carried out radiochemical separations with 100 μg carrier and used spectrophotometric methods for determining chemical yields. Precipitations were made with the help of several milligrams of non-isotopic carriers which were then separated from the wanted nuclide and its isotopic carrier at appropriate stages of the analysis. This technique is of somewhat limited application and the more extensive use of ion-exchange and solvent extraction procedures would probably be more fruitful at the 100-μg level.

Another requirement for radiochemical analysis with 100-μg quantities of carriers is greater sensitivity in chemical yield methods. To retain the desirable feature of replication of chemical yield determinations methods are required which will give the required accuracy of 1–2% with about 5 μg of element. It is hoped to describe a suitable procedure based on micro-coulometry in a forthcoming paper.

SUMMARY

Techniques used at A.W.R.E. during the past 6 years for the radiochemical analysis of mixtures of active nuclides using 0.5- to 1-mg quantities of carrier are described and their advantages discussed. Micro-methods are listed for chemical yield determinations by spectrophotometry and micro-titration, and details are given for the micro-titration of a number of elements with EDTA, using a spectrophotometric end-point. A special fitment is described to enable the Unicam SP600 spectrophotometer to be used for micro-titrations. Some values are given for the coefficients of variation obtained in typical chemical yield methods and in overall radiochemical determinations of ^{99}Mo, ^{111}Ag, ^{115}Cd and ^{140}Ba.

RÉSUMÉ

Les auteurs font un exposé des techniques utilisées au cours de ces six dernières années pour leurs recherches dans le domaine de l'analyse radiochimique de mélanges de radio-isotopes. Des micro-méthodes titrimétriques et spectrophotochimiques sont proposées.

ZUSAMMENFASSUNG

Es wird ein Ueberblick gegeben über die in den vergangenen 6 Jahren angewandten Methoden bei der radiochemischen Analyse von Gemischen von Radio-Isotopen mit besonderer Berücksichtigung von Spektrophotometrie und Mikrotitrationen mit EDTA.

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Short Communications

La détermination du tungstène en présence de vanadium

Dans un article précédent[1], nous avons recommandé la cinchonine et la β-naphtoquinoline comme réactifs gravimétriques pour la détermination quantitative du tungstène. Comme le vanadium est un élément du même groupe, nous avons étudié l'influence du vanadium sur cette détermination gravimétrique du tungstène.

Nous avons employé une méthode directe analogue à celle indiquée dans l'article mentionné, et obtenu les résultats suivants pour différentes quantités de vanadates en présence de tungstates.

TABLEAU I

Réactif	*Cinchonine*			*β-Naphtoquinoline*		
V/W	*mg* ↓	*mg* V_2O_5	%	*mg* ↓	*mg* V_2O_5	%
2	356.3	40.9	+13.0	354.2	38.8	+12.3
1	337.3	21.9	+ 6.9	336.8	21.4	+ 6.8
0.4	326.5	11.1	+ 3.5	325.9	10.5	+ 3.3
0.2	325.2	9.8	+ 3.1	324.7	9.3	+ 3.0
0.08	323.4	8.0	+ 2.5	322.9	7.5	+ 2.4
0.04	321.1	5.7	+ 1.8	320.6	5.2	+ 1.6

Les résultats démontrent que la présence de vanadium donne lieu à une forte coprécipitation, par laquelle les deux réactifs ne peuvent être employés dans la méthode directe.

Une coprécipitation analogue du molybdène a été observée dans un article précédent[2] et a pu être minimalisée par l'emploi d'une méthode décrite en détail dans l'article mentionné. En employant la même méthode pour des mélanges de tungstates et de vanadates, nous avons obtenu les résultats suivants (Tableau II).

TABLEAU II

V/W	*mg* ↓	*mg* V_2O_5	%
2	173.1	1.0	0.58
0.8	173.0	0.9	0.53
0.4	172.7	0.6	0.35
0.16	172.3	0.2	0.12

Ces résultats démontrent que les phénomènes de coprécipitation du vanadium peuvent être minimalisés en effectuant une double précipitation en présence d'acide nitrique et de perhydrol et en employant la β-naphtoquinoline comme réactif. De cette manière, il nous a été possible de déterminer la teneur en tungstène à 0.6% près en présence d'une quantité double de vanadium.

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[1] A. CLAEYS, *Anal. Chim. Acta*, 17 (1957) 360.
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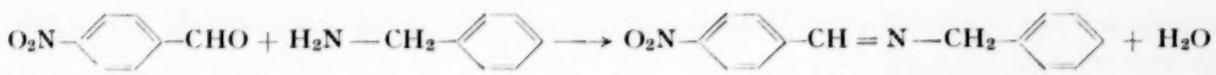
Reçu le 23 janvier 1961

Spot test for benzylamine and *p*-nitrobenzaldehyde*

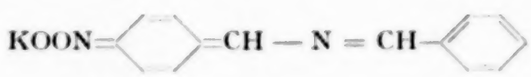
ISOMERIZATION EFFECTS THROUGH FORMATION OF A *p*-QUINOID NITRONIC ACID

If a colorless diluted alcoholic solution of *p*-nitrobenzaldehyde and benzylamine is treated with alkali hydroxide and warmed, an intense red-brown color appears. The color reaction is obviously due to the formation of the Schiff base (I) that was first isolated by INGOLD AND PIGGOT[1]:



(I)

This product undergoes prototropic rearrangement in the presence of alkalis to give a *p*-quinoid nitronic acid salt (II):



(II)

The intense color quality of (II) doubtless is due to its chain of *p*-quinoid and conjugated double bonds.

Since all of the reactions essential to the formation of the highly colored alkali salts of the *p*-quinoid nitronic acid occur rapidly and with small amounts, a spot test for the detection of benzylamine and *p*-nitrobenzaldehyde has been developed on this basis.

Detection of benzylamine

A drop of the test solution, in alcohol if possible, is treated in a micro test tube with a drop of a saturated alcoholic solution of *p*-nitrobenzaldehyde and kept at 80° in a preheated water bath. After 5 min a drop of 2% alcoholic sodium hydroxide solution is added. If the response is positive, a brown-red color appears.

Limit of identification: 10 μg benzylamine.

Considerable quantities of ethylenediamine**, *p*-aminophenol or hydrazine derivatives a free NH_2-group may not be present since they form condensation products with *p*-nitrobenzaldehyde which likewise yield colored salts of quinoid nitronic acids with alkali hydroxide.

Detection of p-nitrobenzaldehyde

A drop of the test solution is treated in a micro test tube with a drop of benzylamine and warmed for 5 min in a water bath. If *p*-nitrobenzaldehyde was present, a red

* Translated by Ralph E. Oesper, University of Cincinnati.

** Ethylenediamine can be detected through its color reaction with rhodizonic acid[2].

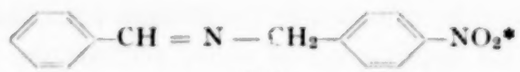
or pink color appears when a drop of 2% alcoholic potassium hydroxide solution is added.

Limit of identification: 1 μg *p*-nitrobenzaldehyde.

This color reaction is not shown by *o*- and *m*-nitrobenzaldehyde or by 2,4-dinitrobenzaldehyde.

In neither test is it permissible to use the now popular solvent, dimethylformamide, since it gives a color reaction with nitro compounds.

The chemistry of the test here described deserves attention because it leads to a case of hitherto unique isomerization. It is obvious that the salt (II) may also be obtained through prototropic rearrangement of the Schiff base of benzaldehyde and *p*-nitrobenzylamine (Ia), which is an isomer of the Schiff base (I), as shown by the following formula:



(Ia)

Consequently it was logical to expect that treatment of the alkali salt(II) with dilute acid would produce initially a mixture of the two isomeric Schiff bases (I) and (Ia), from which by acid hydrolysis there will result the regeneration of all of the compounds necessary to the production of both the isomers (I) and (Ia), namely benzylamine, *p*-nitrobenzaldehyde, benzaldehyde, *p*-nitrobenzylamine. This actually is the case as shown by the following trial with the pair *p*-nitrobenzaldehyde–benzylamine.

A micro test tube was used. Several cg of *p*-nitrobenzaldehyde and benzylamine in alcohol were warmed briefly; alkali hydroxide was added, and the system was then allowed to stand for 1 h. The resulting brown-red solution was then warmed to 40° along with dilute hydrochloric acid, and the mouth of the test tube was covered with a disk of filter paper moistened with an ether solution of benzidine. A yellow stain appeared on the reagent paper; it was due to the Schiff base formed from the benzidine and the benzaldehyde vapors. *p*-Nitrobenzaldehyde does not volatilize under these conditions.

The isomerization through formation of alkali salts of quinoid nitronic acids and their acid decomposition indicates possibilities for preparation procedures directed toward the obtaining of substituted *p*-nitrobenzylamines.

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Received January 17th, 1961

* This Schiff base has also been isolated by INGOLD AND PIGGOT[1]. Its melting point is 71°, in contrast to 56° of its isomer.

Observations on the thermal decomposition of cupric acetate monohydrate

The thermal decomposition of cupric acetate monohydrate has been studied thermogravimetrically by DUVAL[1]. The elimination of water of hydration was shown by a weight loss starting at 107° and concluding at 167°. Further, a complex reaction was reported which was interpreted to result in the formation of copper and cupric oxide, and was initiated at 270° and was complete by 296°. A subsequent slow weight gain up to 510° was associated with the oxidation of metallic copper.

This reaction appeared to be unusual as the copper coexisted in the divalent state and as the free metal. The application of other techniques — differential thermal analysis, X-ray analysis, and mass spectrometry — to the phenomenon could shed more light on the thermal decomposition.

EXPERIMENTAL

The differential thermal analysis apparatus employed was of two types: (*1*) that manufactured by the R. L. STONE Co.[2], Austin, Texas, and (*2*) that described by HILL, SCHACHER AND MURPHY[3]. The latter equipment permitted the analysis of the gaseous products evolved during the reaction to be collected and analyzed. Good agreement was obtained with thermograms produced with both equipments. The thermograms were obtained from approximately 20 mg of material employed as a sandwich in alumina. Heating rates of approximately 10° per minute were employed. An air atmosphere was employed in all cases, the pressure being approximately 0.5 mm. X-ray diffraction patterns were obtained on a General Electric Model XRD-5 X-ray spectrograph. Gas analyses were performed using a General Electric Analytical Mass Spectrometer. Materials employed were of a C.P. grade.

DISCUSSION

The thermogram of cupric acetate monohydrate, Fig. 1, shows the release of water of crystallization starting at about 145° and peaking at approximately 180°. A series

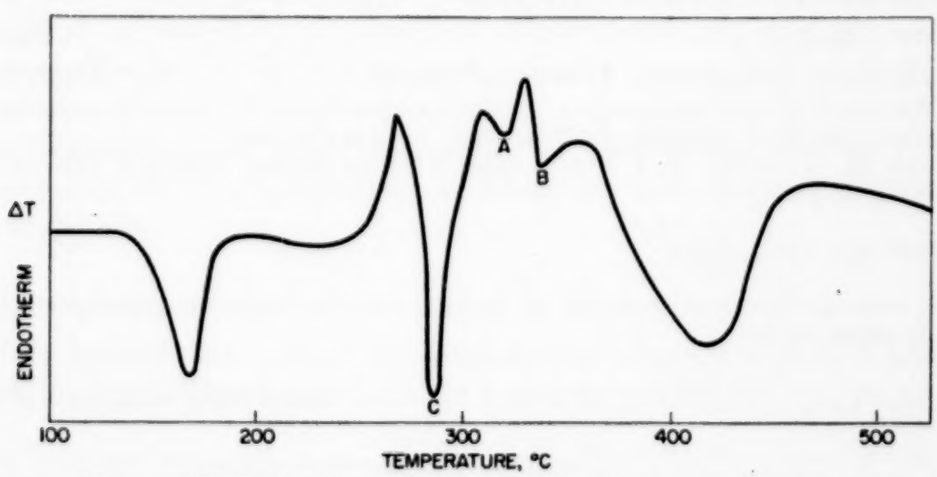

Fig. 1. Differential thermogram, cupric acetate monohydrate.

of complex reactions were initiated in the range 245–450°. Thermograms for cupric oxide and its 50–50 mole % mixture with copper showed no thermal effects in the temperature range covered by Fig. 1.

A gas sample was obtained from the second differential thermal analysis apparatus at point C indicated on the thermogram. The mass spectrum indicated the gas to be principally carbon dioxide with a substantial amount of water. Very small quantities of acetone and methane were also present. It was interesting to observe that there was no residual oxygen in the air background, indicating occurrence of an oxidation reaction with the unusual decomposition.

X-ray analyses were made of sample holder residues obtained by stopping the differential thermal runs at points A and B. The residue at B gave only lines corresponding to cupric oxide. At point A, the X-ray diffraction pattern corresponded to a mixture of cuprous oxide and copper metal.

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Anal. Chim. Acta, 24 (1961) 496–497

Separation of niobium and tantalum by N-benzoyl-N-phenylhydroxylamine

N-Benzoyl-N-phenylhydroxylamine was used by MAJUMDAR AND MUKHERJEE[1] for the separation and gravimetric determination of niobium and tantalum. They recommended a pH range of 3.5 to 6.5 for the complete precipitation of niobium and a pH below 1.5 for the precipitation of tantalum from tartrate solutions.

TABLE I

pH of ppln. of Nb	*Nb_2O_5 taken, mg*	*Ta_2O_5 taken, mg*	*Coagulation period, min*	*Wt. of Nb complex, mg*	*Nb_2O_5 found, mg*	*Ta_2O_5 found, mg*
3.0	8.7	12.7	30–35	—	8.2	12.84
3.5	8.7	12.7	30–35	48.4	8.635	12.6
4.0	8.7	12.7	30–35	48.6	8.67	12.6
4.0	12.4	5.4	30–35	—	12.40	5.4
4.5	8.7	12.7	25–30	48.8	8.7	12.68
5.0	8.7	12.7	25–30	48.8	8.7	12.73
5.5	8.7	12.7	25–30	48.83	8.7	12.70
6.0	8.7	12.7	25–30	48.6	8.67	12.72
6.5	12.4	5.4	30–35	—	12.2	5.6

In a recent communication[2], LANGMYHR AND HONGSLO suggested that the pH range could profitably be narrowed from 3.5–6.5 to 4.5–5.0; this latter pH range is said to give better results for separation while the former may cause precipitation of hydrous oxide and needs a longer coagulation period. We have now checked that the pH range, as suggested by MAJUMDAR AND MUKHERJEE, gives quite good results within the specified coagulation period; moreover, there is no possibility of the precipitation of hydrous oxide, even when the niobium or the tantalum solution is made ammoniacal. The results shown in Table I confirm these observations.

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[1] A. K. MAJUMDAR AND A. K. MUKHERJEE, *Anal. Chim. Acta*, 19 (1958) 23; 21 (1959) 245.
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Anal. Chim. Acta, 24 (1961) 497–498

Voltammetric determination of antioxidants at the wax-impregnated graphite electrode

The wax-impregnated graphite electrode is well-known in the analysis of antioxidants[1–4]. A real improvement was suggested by MORRIS AND SCHEMPF[4], who made very reproducible electrode surfaces on a manual lathe.

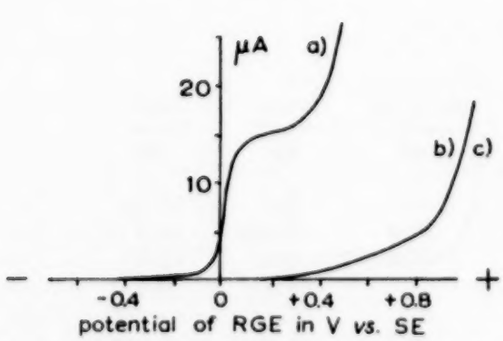

Fig. 1. Anodic oxidation of 2,6-di-*tert.*-butyl-*p*-cresol at the RGE in (a) basic solution, (b) weakly acidic solution, and (c) acidic solution. See text for compositions. RGE = Rotating wax-impregnated graphite electrode; SE = Silver–silver chloride electrode.

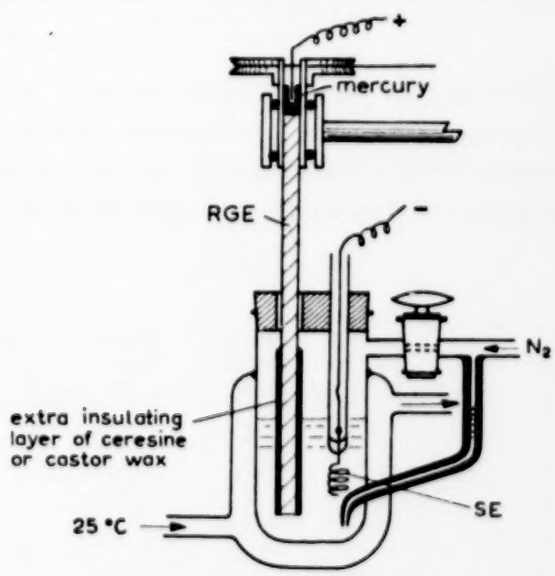

Fig. 2. Voltammetric cell. RGE, SE — see legend to Fig. 1.

As far as we know, investigation of the influence of the pH on the mechanism of oxidation at the electrode has been limited to the lower pH values. A possible explanation for this may be that the anodic potential range is much smaller in basic than in acidic or neutral supporting solutions. However, the oxidation potentials of anti-oxidants of both the phenolic and the amino type are shifted in the same sense (*i.e.* more negative at higher pH-values), since hydrogen ions are always involved in the anodic oxidation process. Therefore, in most cases a supporting electrolyte of higher pH can be used and recommended, especially for anti-oxidants of the phenolic type because the reaction becomes more reversible, with the result that the wave form is considerably improved (see Fig. 1).

Rotation of the electrode at a speed of *ca.* 500 rev./min affects both the reproducibility and the sensitivity favourably (see Fig. 2 for instrumental details). Under these conditions the wave form equals the normal polarographic form, whilst concentrations down to $5 \cdot 10^{-7}$ *M* can be detected.

EXPERIMENTAL

Composition of the supporting electrolyte

(*a*) Place 5 ml of $5 \cdot 10^{-4}$ *M* 2,6-di-*tert.*-butyl-*p*-cresol in methanol, 3 ml of lithium chloride (5 g per 100 ml methanol) and 5 ml of 0.1 *M* potassium hydroxide in methanol in a 25-ml volumetric flask. Fill up with methanol.

(*b*) and (*c*) Prepare the solution as described in (*a*) with the exception of the potassium hydroxide. Replace the latter by 5 ml of 0.1 *M* boric acid in methanol (*b*) or by 0.5 ml of 0.1 *M* hydrochloric acid in methanol (*c*). The water content of the methanol should be as low as possible.

Summary of the analytical procedure

Rate of polarization: 0.8 to 0.9 mV per sec. Temperature: 25.0°. Polish the electrodes before each determination with a fine grade of sand paper. Precondition the RGE for 2 min at +0.9 V *vs.* SE((weak)-acidic supporting electrolyte), or at +0.5 V *vs.* SE (basic supporting electrolyte). Removal of oxygen is not essential. Electrolyse the solution to more positive values.

Central Laboratory of the Netherlands State Mines, Geleen (The Netherlands) E. BARENDRECHT

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Received February 3rd, 1961

Revue de livre

Electrochimie Théorique par EUGÈNE ET GENEVIÈVE DARMOIS, Masson & Cie., Paris, 1960, ii + 240 pp., 123 Figs., cartonné toile demi-souple, 39NF.

Bien que sous forme relativement succinte, ce livre est indiscutablement destiné au succès. Il contient l'étude de tous les phénomènes dans lesquels la présence ou le transport de charges électriques sont associés à la matière, quel que soit son état, solide, liquide ou gazeux, qu'elle se présente sous une forme simple, telle que les solutions ou les sels fondus, ou sous une forme plus complexe, telle que les électrolytes colloïdaux.

Les auteurs, loin de se contenter d'exposer tout simplement les données de la bibliographie, procèdent à un examen critique et éclairé des diverses théories en se basant sur un grand nombre de travaux, tout à fait remarquables d'ailleurs, effectués dans leurs laboratoires.

Nous ne pouvons donner ici que les grandes divisions de l'ouvrage: Historique; Conductibilité des électrolytes, sa mesure; Conductibilité équivalente; Mobilité des ions, nombres de transport; Mobilité des ions et viscosité; Force électromotrice des piles, coefficient d'activité des électrolytes; Anomalies des électrolytes forts, dissociation; La théorie de l'interaction ionique et ses perfectionnements; Propriétés irréversibles des électrolytes; Propriétés optiques des solutions électrolytiques, degré de dissociation des électrolytes d'après les méthodes optiques; Propriétés des électrolytes fondus; Retour sur les F.E.M. des piles, électrodes du premier genre, potentiels normaux; Électrodes du deuxième et troisième genres, applications diverses; Piles avec et sans diffusion, diffusion des électrolytes; Étude de la concentration en ion hydrogène; Électrolytes colloïdaux et applications; Électrolytes solides semiconducteurs; Polarisation des électrodes, mesure de la F.E.M. de polarisation, polarographie; Surtension d'activation, dégagement des gaz et dépôt des métaux; Anodes solubles, passivité; Double couche au contact d'un métal et d'un électrolyte, électrocapillarité; Phénomènes électrocinétiques, électroosmose, électrophorèse, applications; Électrochimie des gaz; Applications analytiques de l'électrochimie; Galvanoplastie et dépôts métalliques; Technique des différents dépôts galvaniques.

Pour terminer, nous nous faisons un plaisir de signaler que l'*Electrochimie Théorique* d'EUGÈNE et de GENEVIÈVE DARMOIS est un livre qui, grâce à son caractère vivant, incite à la reflexion et que, par cela même, il pourra donner des nouvelles idées fécondes aux chercheurs dans cette branche, auxquels EUGÈNE DARMOIS ne peut, hélas! plus se joindre. Qu'il nous soit permis de rendre un hommage ému à la mémoire du grand chercheur que fut ce savant.

Une recommandation du livre serait superflue, car ceux qui l'ont déjà étudié ne pourraient que très difficilement s'empêcher de s'exprimer en faveur d'une oeuvre aussi remarquable.

I. KAPÉTANIDIS (Genève)

DETECTION OF SELENIUM IN ORGANIC SPOT TEST ANALYSIS*

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(Received December 6th, 1960)

Studies of the reactions of organic selenium compounds revealed the need for a reliable test for selenium which if possible should be rapid and suitable for use on a micro scale. No such procedure could be found in the literature and accordingly a study was organized in which organic compounds of selenium were subjected to reductive or oxidative cleavage by the wet or dry method with the hope of arriving at inorganic selenium compounds which are suitable for the methods of inorganic spot test analysis.

In case of a reduction to the gaseous hydrogen selenide, it seemed likely that reaction of this product with sulfurous acid or iodine to yield elemental selenium could be utilized for the purpose at hand. However, it turned out that the desired reduction by warming organic selenium compounds in acid or alkaline milieu with Devarda alloy, zinc, or Raney nickel did not proceed. Although indications of a reaction leading to elemental selenium or hydrogen selenide were observed with Raney nickel, the conditions could not be discovered for a reliable test for selenium. Attempts to produce hydrogen selenide by sintering with sodium formate, through the reaction $2\ NaCOOH \rightarrow (COONa)_2 + 2\ H^\circ$ which yields hydrogen at 250° were completely unsatisfactory. This finding was remarkable in that only reduction to elemental selenium was obtained whereas organic sulfur compounds of all kinds yield hydrogen sulfide when sintered with sodium formate. A rapid spot test for organically bound sulfur is based on this fact[1].

The efforts to arrive at oxygenated selenium compounds through oxidation by the dry or wet methods were more successful. Such products react rapidly with hydrazine in acidic surroundings and on warming to give red elemental selenium:

$$SeO_3^{-2} + NH_2NH_2 + 2\ H^+ \rightarrow Se^\circ + N_2 + 3\ H_2O$$

Sintering with potassium permanganate has been recommended for the quantitative determination of oxyacid-forming nonmetals in organic compounds[2] and this procedure does yield alkali selenite or selenate when applied to selenium-bearing organic compounds. The sintering can be accomplished with tiny amounts in a micro test tube. The cold residue is heated with 1 or 2 drops of concentrated hydrochloric acid until a clear solution results. When the latter is treated with some solid hydrazine sulfate or chloride, red elemental selenium precipitates. The limits of identification are at quantities of materials which correspond to a content of 10–20 μg selenium.

Another kind of oxidative decomposition (in the wet way) is to warm the sample

* Translated by RALPH E. OESPER, University of Cincinnati.

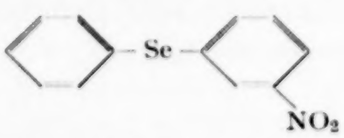
with potassium persulfate and sulfuric acid in the presence of a little silver nitrate as catalyst[3]. The identification limits were satisfactory but certain selenium compounds proved to be very resistant to this treatment and so required several repetitions of the wet oxidation by persulfuric acid. Another disadvantage of this oxidation is that it is not likely to accomplish the objective because the catalytic action of the silver ions is incapacitated by the formation of silver halide in the case of organic compounds containing halogens.

Much better and completely reliable results are achieved by means of wet oxidation with perchloric acid, which was studied in extenso by SMITH[4] and recommended for the decomposition of organic materials. Perchloric acid, which is not an oxidant in aqueous solution, forms an azeotropic mixture (72.5% $HClO_4$) with water. The mixture boils at 170°. At this temperature, perchloric acid is a remarkably powerful and rapid oxidant and is highly suitable for liberating the metals in organo-metallic compounds. As shown by SMITH, organic-bound sulfur and phosphorus are converted into sulfuric or phosphoric acid. Our studies have shown that warming arsenic- or selenium-bearing organic compounds with perchloric acid rapidly produces arsenic or selenic acid. Since perchloric acid does not react with hydrazine in aqueous solution, a combination of the oxidative decomposition with perchloric acid and the redox reaction of the resulting selenic acid with hydrazine can lead to a specific test for organically bound selenium. The heating with perchloric acid is without danger; explosive decompositions were never encountered in more than 100 trials. The test can be accomplished in around 10 min.

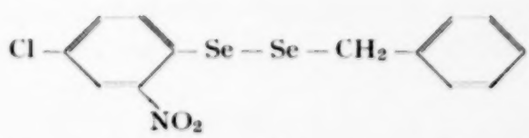
PROCEDURE

A small quantity of the test material or the evaporation residue from 1 drop of its solution in water, alkali hydroxide, alcohol, etc. is placed in a micro test tube and then 1 drop of concentrated (70–72%) perchloric acid is introduced. The mixture is gradually heated to 205° in a glycerol bath. After about 3 min at this temperature, the contents of the test tube are cooled, a drop of a saturated hydrazine sulfate solution is added, and the mixture warmed in a boiling water bath. Depending on the quantity of selenium present, a red precipitate or a pink coloration appears.

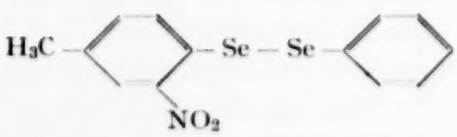
A positive response was obtained with:



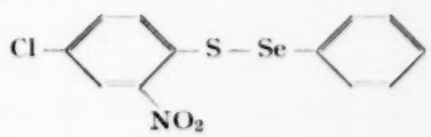
6 μg Phenyl(*m*-nitrophenyl)selenide



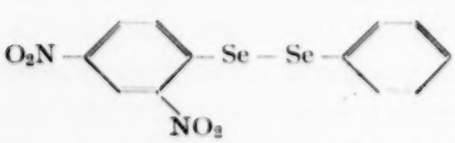
5 μg Benzyl(2-nitro-4-chlorophenyl)diselenide



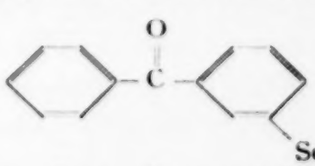
5 μg Phenyl(2-nitro-4-methylphenyl)diselenide



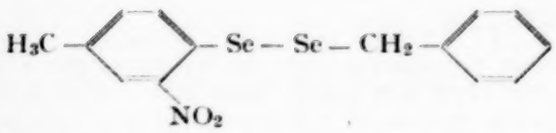
30 μg Phenyl(2-nitro-4-chlorophenylthio)selenide



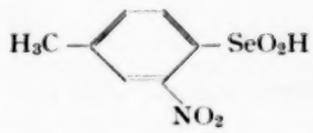
5 μg Phenyl(2,4-dinitrophenyl)diselenide



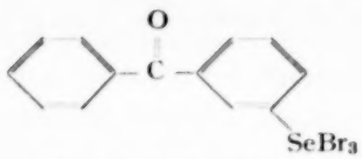
5 μg *o*-Benzoylbenzeneseleninic acid



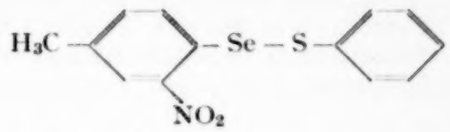
5 μg Benzyl(2-nitro-4-methylphenyl)diselenide



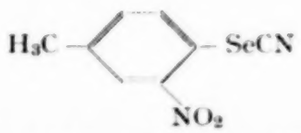
5 μg 2-Nitro-4-methylbenzeneseleninic acid



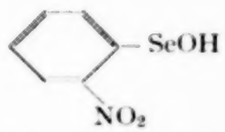
30 μg 3-Benzoylphenylselenium tribromide



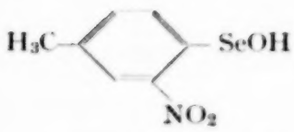
6 μg Phenylthio(2-nitro-4-methylphenyl)selenide



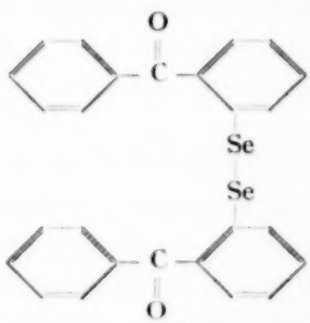
5 μg 2-Nitro-4-methylphenylselenocyanate



10 μg 2-Nitro-*p*-tolueneselenenic acid



5 μg 2-Nitrobenzeneselenenic acid



30 μg bis-(2-Benzoylphenyl)diselenide

5 μg bis-(2-Naphthyl)selenide

This success in the qualitative detection of selenium in organic materials leads to the expectation that the oxidative decomposition with perchloric acid may likewise be of value in the quantitative determination of selenium in organic materials.

ACKNOWLEDGEMENT

The author is indebted to Mrs. E. KERDMAN-LIBERGOTT for carrying out many of the experiments.

SUMMARY

A test is described for the detection of selenium in organic compounds. It is based on the oxidative decomposition with hot concentrated perchloric acid to yield selenic acid, which reacts with hydrazine to give red elemental selenium. Microchemical limits of identification are reached within the technique of spot test analysis.

RÉSUMÉ

Une réaction à la touche est proposée pour l'identification du sélénium dans des composés organiques. La substance à analyser est attaquée par l'acide perchlorique; l'acide sélénique formé peut alors réagir avec l'hydrazine pour donner du sélénium élémentaire rouge.

ZUSAMMENFASSUNG

Zum Nachweis von Selen (Tüpfelprobe) in organischen Substanzen wird die Substanz mit Perchlorsäure zerstört und das Selen nach Reduktion mit Hydrazin durch seine rote Farbe nachgewiesen.

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DETERMINATION OF AMINES AND ALKYL PHOSPHATES IN KEROSENE SOLUTIONS CONTAINING URANIUM AND SULPHURIC ACID

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(Received September 20th, 1960)

INTRODUCTION

Mixtures of alkyl phosphoric acids and amines in kerosene solution have been used for the extraction of uranium and vanadium from leach solutions[1]. Experiments have been carried out in this laboratory on the extraction of uranium from leach solutions by tertiary amine-alkyl phosphoric acid-tributyl phosphate mixtures in kerosene solution. Methods for the determination of these constituents were required for a complete study of the extraction. A search of the available literature failed to disclose any suitable methods.

EXPERIMENTAL

Determination of amine

Determinations of amine in kerosene solutions containing uranium and sulphuric acid have been carried out in this laboratory for several years. Uranium and sulphuric acid are removed by shaking the kerosene solution with calcium hydroxide. Sulphuric acid is precipitated as calcium sulphate and uranium is adsorbed on the calcium hydroxide. The solids are removed by filtration, and amine is determined on the filtrate by titration, in chloroform solution, with a non-aqueous solution of hydrochloric acid. Thymol blue is used as the indicator.

Application of this method to the determination of amine in the presence of alkyl phosphoric acids gave high results. The alkyl phosphoric acid caused a turbidity in the filtrate which could not readily be removed. This turbidity gave an alkaline reac-

tion, causing high amine results. The use of calcium acetate in place of the calcium hydroxide overcame this problem, and also removed sulphuric acid as insoluble calcium sulphate. Uranium, however, was not completely removed.

Extraction of uranium can readily be achieved by shaking the kerosene solution with a 20% v/v solution of sulphuric acid before shaking with calcium acetate. After removal of uranium and sulphuric acid, the amine is titrated in chloroform solution, with a dioxan solution of perchloric acid, using thymol blue as the indicator. Tributyl phosphate does not interfere. The reactions occurring are shown in the following equations:

$$(R_3N)_2.H_2SO_4 + (CH_3COO)_2Ca = CaSO_4 + 2\ R_3N.CH_3COOH$$

$$R_3N.CH_3COOH + HClO_4 = R_3N.HClO_4 + CH_3COOH$$

Determination of alkyl phosphoric acid

A mixture of an amine and an alkyl phosphoric acid in chloroform solution behaves as a solution of a dipolar molecule. Consequently, titration of this solution with a strong acid determines the amine, and titration of the same solution with a strong base determines the alkyl phosphoric acid. An excellent indicator for these titrations is thymol blue, having two colour changes, red to yellow at pH 1.7, and yellow to blue at pH 8.9. In the absence of any other acids or bases, this provides a rapid and accurate method for the determination of amine and alkyl phosphoric acid.

Sulphuric acid, if present, must be removed before the alkyl phosphate can be determined. Calcium acetate cannot be used, as it removes some of the alkyl phosphate, giving low results. The problem was overcome by using sodium methoxide, to precipitate the sulphuric acid as sodium sulphate, which is insoluble in chloroform solution.

When a sodium methoxide solution is added to a chloroform solution containing sulphuric acid, amine and an alkyl phosphoric acid, the following reactions occur:

$$(R_3N)_2.H_2SO_4 + 2\ CH_3ONa = 2\ R_3N + Na_2SO_4 + 2\ CH_3OH$$

$$H_2RPO_4 + 2\ CH_3ONa = Na_2RPO_4 + 2\ CH_3OH$$

$$HR_2PO_4 + CH_3ONa = NaR_2PO_4 + CH_3OH$$

$$H_2SO_4 + 2\ CH_3ONa = Na_2SO_4\downarrow + 2\ CH_3OH$$

When thymol blue is used as the indicator, excess of sodium methoxide is indicated by a colour change of yellow to blue. The excess sodium methoxide can then be back-titrated with perchloric acid to a blue to yellow end-point. At this point sulphuric acid has been removed from solution as the neutral sodium sulphate which does not interfere in the subsequent titrations. Amine is present in solution as the free amine, and the alkyl phosphoric acid as the sodium salt. When titration with perchloric acid is continued to a yellow to red end-point, both amine and alkyl phosphoric acid are titrated according to the equations:

$$R_3N + HClO_4 = R_3N.HClO_4$$

$$Na_2RPO_4 + 2\ HClO_4 = H_2RPO_4 + 2\ NaClO_4$$

$$NaR_2PO_4 + HClO_4 = HR_2PO_4 + NaClO_4$$

The difference between the volume of perchloric acid used to titrate the amine plus alkyl phosphoric acid, and the amine alone, is equivalent to the amount of alkyl phosphoric acid.

Concentrations of amine and alkyl phosphoric acid are expressed in molarity, in order to simplify the calculations.

Determination of tributyl phosphate

Tributyl phosphate is determined from the difference between the total amount of phosphorus in the solution and that due to the alkyl phosphoric acid. The method used for the determination of total phosphorus has been used successfully in this laboratory for several years.

Determination of amine and phosphoric acids

Reagents

Thymol blue solution, 0.5% w/v in ethyl alcohol. Calcium acetate and chloroform, analytical-reagent grades. Sodium methoxide solution, approx. 0.1 *N*. Dissolve 2.5 g of sodium metal in 1 l of methyl alcohol. Perchloric acid solution, 0.1 *N*. Dilute 8.4 ml of perchloric acid (70%) to 1 l with dioxan. Standardise by any convenient method.

Procedure

Transfer about 30 ml of sample to a 125-ml separating funnel, and add about 20 ml of 20% v/v sulphuric acid. Shake for 1 min, allow the phases to separate, and discard the aqueous phase. Repeat this extraction twice. Filter the organic phase through a double coarse filter paper. Add to a 5-ml aliquot of the filtrate, in chloroform solution, a few drops of thymol blue solution, and sodium methoxide solution until the solution colour changes to a deep blue. Add perchloric acid solution to a blue to yellow end-point. Titrate from this point with the perchloric acid solution to a yellow to purple end-point (Titre *A*).

To the remainder of the uranium-free filtrate add about 5 g of calcium acetate and shake for 1 min. Filter through a coarse filter paper. Titrate a 5-ml aliquot of the filtrate, in chloroform solution, with the perchloric acid solution to a yellow to purple end-point, using thymol blue indicator (Titre *B*).

$$\text{Amine molarity} = \frac{B \times \text{normality of } HClO_4}{5}$$

$$\text{Alkyl phosphoric acid molarity} = \frac{(A - B) \times \text{normality of } HClO_4}{5}$$

Determination of tributyl phosphate

Place 1 g of magnesium oxide in a small porcelain crucible, and tap to consolidate. Pipette 2 ml of the sample onto the magnesium oxide, and place another 1 g of magnesium oxide on top of the sample. Tap to consolidate. Heat the crucible over a burner until the organic vapours ignite. Remove from the burner and allow to burn until the flame is extinguished. Heat the crucible over a burner until all the carbon has been burned off. Cool and transfer the magnesium oxide to a beaker containing a few ml of water. Add 5 ml of perchloric acid to the crucible, and 3 ml to the beaker.

Heat the crucible until strong fumes are evolved, transfer the contents to the beaker and rinse the crucible into the beaker with the water. Heat the beaker to dissolve the magnesium oxide. The phosphorus may be determined by any suitable method. In this laboratory, a molybdovanadophosphoric acid colorimetric method is used.

$$\text{TBP molarity} = \frac{\text{g/l total P} - \text{g/l P from alkyl phosphoric acid}}{31}$$

RESULTS

In these experiments, the amine used was a trifatty amine; the alkyl phosphoric acids used were monoheptadecyl phosphoric and di-2-ethyl-hexyl phosphoric acids. These reagents were only of technical grade, and it was found necessary to determine the apparent molecular weights of each, in order to make up solutions of known molarity. Since very accurate molecular weights were not necessary, they were determined by titrating weighed amounts of the amine and alkyl phosphoric acids with standard solutions of perchloric acid and sodium methoxide respectively. Thymol blue was used as the indicator. Molecular weights are given in Table I. The tributyl phosphate was pure, and the molecular weight used was the theoretical one.

TABLE I

MOLECULAR WEIGHTS OF AMINE AND ALKYL PHOSPHORIC ACIDS

	Calc. mol. wt.	*Apparent mol. wt.*
T.F.A.	—	450
M.H.D.P.A.	336	449
D.E.H.P.A.	322	316

TABLE II

DETERMINATION OF AMINE, ALKYL PHOSPHORIC ACIDS AND TRIBUTYL PHOSPHATE MIXTURES IN KEROSENE SOLUTION*

Amine molarity found	*MHDPA molarity found*	*TBP molarity found*
0.102	0.200	0.106
0.101	0.202	0.107
0.103	0.203	0.109
0.100	0.199	0.109
0.103	0.203	0.104

Molarities added: Amine 0.102, MHDPA 0.202, TBP 0.108

Amine molarity found	*DEHPA molarity found*	*TBP molarity found*
0.196	0.100	0.099
0.198	0.099	0.099
0.199	0.103	0.098
0.196	0.102	0.100
0.200	0.102	0.099

Molarities added: Amine 0.198, DEHPA 0.101, TBP 0.100

* Containing uranium and sulphuric acid.

Kerosene solutions containing known amounts of amine, alkyl phosphoric acid and tributyl phosphate were shaken with a dilute sulphuric acid solution containing uranium. Uranium and sulphuric acid were extracted from the aqueous into the organic phase. After separation of the two phases, the amine, alkyl phosphoric acid and tributyl phosphate were determined by the methods described. Results are given in Table II.

SUMMARY

Methods for the determination of amines, alkyl phosphoric acids and tributyl phosphate in kerosene solutions containing uranium and sulphuric acid are described. Amine and alkyl phosphoric acid are determined volumetrically, after removal of interferences, by titration in chloroform solution with a dioxan solution of perchloric acid. Tributyl phosphate is determined by difference between the total phosphorus and the phosphorus from the acid alkyl phosphoric acid.

RÉSUMÉ

L'auteur décrit une méthode pour le dosage d'amines, d'acides alcoylphosphoriques et de tributylphosphate dans des solutions de kérosène, renfermant de l'uranium et de l'acide sulfurique. L'amine et l'acide alcoylphosphorique sont dosés volumétriquement par l'acide perchlorique, en solution dans le dioxane. Quant au tributylphosphate, il est déterminé par différence entre le phosphore total et le phosphore de l'acide alcoylphosphorique.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Aminen, Alkylphosphorsäuren und Tributylphosphat in Kerosin Lösung, die ausserdem noch Uran und Schwefelsäure enthält. Amine und Alkylphosphorsäuren werden in Chloroformlösung mit einer Dioxan-Perchlorsäurelösung titriert. Die Differenz zwischen der Gesamtmenge Phosphor und der Alkylphosphorsäure ergibt die Menge an Tributylphosphat.

REFERENCE

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SOME POSSIBLE APPLICATIONS OF MASS SPECTROMETRY TO ACCOUNTING PROBLEMS IN CHEMICAL PROCESSING PLANTS

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INTRODUCTION

The overall accuracy of accounting analyses made for fissile material in a chemical processing plant will usually be limited by difficulties associated with the determination of a valid "plant input figure", for this often involves analyses of the plant feed solution. The isotopic dilution method using solid source mass spectrometry is capable of providing very precise analyses for plutonium[1] or uranium[2,3] in a given solution, but in the application of such a method to the feed solution of a chemical processing plant the overall precision would almost inevitably be controlled by larger errors associated with the determination of sample aliquots, volumes of plant solution, or dilution factors under remote or semi-remote handling conditions. Clearly much would be gained if the isotopic dilution methods could be applied in such a way that either plant sampling errors are eliminated, or at least their significance minimised. The present paper considers this possibility in two typical cases: accounting for plutonium in a plant processing natural uranium fuel elements, and accounting for ^{235}U in enriched uranium–aluminium alloy fuel elements. Where appropriate, published data for the Windscale and Dounreay plants have been used to define typical solution conditions[4,5].

DETERMINATION OF PLUTONIUM IN NATURAL URANIUM FUEL ELEMENTS

Introduction

A previous paper[1] described the determination of plutonium using a ^{242}Pu tracer. Results were obtained for several test solutions and these indicated a precision (1σ) of 0.2% for a single determination. In calculating this figure errors introduced by the dilution of sample and standard were assessed at $\sim$0.1%, so in this case the elimination of these dilution errors could only reduce the overall precision to $\sim$0.18%. However, this latter figure will still include random errors associated with weighing the aliquots of dilute sample and tracer mixed for each determination, and moreover, in this instance the samples were diluted under nearly ideal conditions. In considering the use of this method on a routine basis for the control of a chemical plant it must be recognised that dilution errors could easily be much larger, and in addition uncertainties will be introduced in relating the initial aliquot to the total volume of solution in the plant, and by evaporation of solutions, etc. Once the overall sampling error rises above 0.2% it will be this factor, and not the mass spectrometric analyses, which will control the precision of results obtained for accounting purposes; for example, the

overall precision quoted for the isotopic dilution method (including remote pipetting) used for uranium in the Idaho Chemical Processing Plant is ~2%, whereas the errors involved in mass analyses alone were much smaller[3,6].

In principle sampling errors could be completely eliminated from a plutonium determination by dissolving a batch of fuel elements containing a known quantity of uranium, and then making a determination of the [Pu]/[U] concentration ratio for a small aliquot of the solution. Fuel elements may consist of rods of natural uranium in aluminium or Magnox cans; the rods are "de-canned" by means of a die and a hydraulic ram, and are then transferred to the chemical plant[4]. The mass of uranium rods determined either by weighing after "de-canning", or from the fuel element production data, and corrected for the small quantity of uranium consumed by fission or by conversion to plutonium could give the total uranium input to the plant. The product of this quantity and the appropriate [Pu]/[U] ratio should then give the total plutonium input to the plant. In practice a plant may be operated under continuous conditions so plant sampling errors may still be involved in obtaining a representative aliquot for analysis; however the effect of this should be very much smaller in a [Pu]/[U] ratio measurement than is the case when an aliquot is taken for a direct plutonium determination.

The work to be described represents an assessment of the errors involved in a determination of the [total Pu]/[total U] concentration ratio by a single mass spectrometric analysis. The samples used were similar to those described previously[1] and contained uranium, plutonium and fission products. Since this work was completed a similar ratio procedure has been described, but using less precise analytical methods, namely radiometric analyses for plutonium, and density or X-ray photometric determinations for uranium[7].

Outline of the method

The basis of the present ratio method can be illustrated by examining the equations used to calculate Pu and U concentrations. If an aliquot derived from a plant solution is mixed with an aliquot of ^{242}Pu tracer, the concentration of total plutonium in the original solution, $[Pu]_s$, may be found from the following equation:

$$[Pu]_s = [^{242}Pu]_t \cdot \frac{\text{mass tracer aliquot}}{\text{mass sample aliquot}} \cdot \frac{M_{239/242} - T_{239/242}}{(\text{mass percentage } ^{239}Pu)_s} \cdot \frac{239}{242} \cdot D \qquad (1)$$

where the subscripts s and t refer to the sample under analysis and the ^{242}Pu tracer; $M_{239/242}$ represents the $^{239}Pu/^{242}Pu$ ratio determined by mass spectrometry for the mixture, and similarly $T_{239/242}$ for the tracer alone; D is the dilution factor for the sample.

Similarly the concentration of total uranium, $[U]_s$, may be determined by adding an aliquot of ^{233}U tracer and then using eqn. (2), the definitions of terms used being analogous to those for eqn. (1).

$$[U]_s = [^{233}U]_t \cdot \frac{\text{mass tracer aliquot}}{\text{mass sample aliquot}} \cdot \frac{M_{238/233} - T_{238/233}}{(\text{mass percentage } ^{238}U)_s} \cdot \frac{238}{233} \cdot D \qquad (2)$$

Thus if an aliquot of a tracer containing a mixture of ^{242}Pu and ^{233}U is added to a

sample containing both plutonium and uranium, the $[Pu]_s/[U]_s$ ratio is given by eqn. (3), where n is a numerical constant.

$$\frac{[Pu]_s}{[U]_s} = n \frac{[^{242}Pu]_t}{[^{233}U]_t} \cdot \frac{M_{239/242} - T_{239/242}}{M_{238/233} - T_{238/233}} \cdot \frac{(\text{mass percentage } ^{238}U)_s}{(\text{mass percentage } ^{239}Pu)_s} \quad (3)$$

In this equation the masses (or volumes) of sample and tracer solutions, and the dilution factor are eliminated. The first term of the expression, *i.e.* $n[^{242}Pu]_t/[^{233}U]_t$, is obtained by calibration of the mixed tracer against a standard mixture prepared from ^{239}Pu metal and natural uranium; the second term contains either constants for the tracers (Pu, $T_{239/242}$ ~0.005; U, $T_{238/233}$ ~0.0002) or isotopic ratios determined for the mixture of sample and tracer. The third term, consisting of the ratio of the isotopic mass percentages of ^{239}Pu and ^{238}U in the sample under examination, is determined most accurately by taking a second aliquot of sample to which tracer has not been added. However, under certain conditions these quantities may be determined from the mass analysis for the mixture by correction for the quantity of tracer present, and it should then be possible to obtain a value for the following expression by a single mass spectrometric analysis:

$$\frac{M_{239/242} - T_{239/242}}{M_{238/233} - T_{238/233}} \cdot \frac{(\text{mass percentage } ^{238}U)_s}{(\text{mass percentage } ^{239}Pu)_s} \quad (4)$$

Chemical procedure

The chemical procedure used for plutonium has been described in detail elsewhere[1] and only an outline will be given here. A portion of sample is diluted and an aliquot taken containing approximately 0.1 μg Pu (and in this case ~250 μg U). To this is added an aliquot of mixed tracer containing approximately 0.1 μg ^{242}Pu and 250 μg ^{233}U. The dilution factor and the aliquots need not be determined accurately, but approximate values will be required to permit some control over the values of the $^{239}Pu/^{242}Pu$ and $^{238}U/^{233}U$ ratios produced in the mixture. The mixture of tracer and sample is treated with hydroxylamine hydrochloride followed by nitric acid in order to ensure isotopic exchange, and a solution is then prepared in 8 *M* nitric acid. About 2% of this solution is taken directly and evaporated to dryness on a microscope slide; this provides ample uranium (~5 μg ^{238}U and ~5 μg ^{233}U) for a mass analysis. The rest of the solution is applied to a column of deacidite FF; uranium and fission products are washed through with 8 *M* nitric acid, and then plutonium eluted with 0.1 *M* hydroxylamine hydrochloride, 1 *M* hydrochloric acid solution. The eluate containing plutonium is evaporated to small volume in a beaker, and then to dryness on a microscope slide. The uranium and plutonium specimens obtained in this way from any one sample are mounted separately on the two side filaments of a triple filament ion source[8] for a mass spectrometric analysis.

A possible source of error in the uranium determinations could be contamination by natural uranium, either airborne or from reagents. This was examined in two stages by blank determinations. The first was made for the initial part of the chemical treatment which involved ~250 μg ^{238}U; the contamination level was 0.002 μg representing an uncertainty of only 0.001%. The second determination was made

starting at the point at which a 2% aliquot of solution (~5 μg ^{238}U) was taken and prepared for a mass analysis. This gave an upper limit of only 0.00001 μg, which is again insignificant.

Mass spectrometry

Isotopic analyses were made using an A.E.I. Ltd. M.S.5 mass spectrometer, which is a 12" radius of curvature 90° sector single focusing instrument incorporating an electron multiplier. The centre filament of the ion source was heated by an unstabilised power supply; stabilised units were used to heat the side filaments. The two side filaments were heated together while they were being "pre-heated" to minimise hydrocarbon background[9], but thereafter were treated separately. The following procedure was usually used for each mass spectrometric analysis. About 40 ^{239}Pu/^{242}Pu ratios were first recorded; then the collector slit width was reduced and about 10 ^{240}Pu/^{242}Pu and ^{241}Pu/^{242}Pu ratios were recorded at a slower scanning speed. A similar procedure was then used to record ^{238}U/^{233}U (~40) and ^{235}U/^{233}U (~10) ratios, but in this case, to reduce the scanning time, a small resistance was switched into and out of the magnet current circuit in order to change the focused ion from ^{233}U to ^{238}U or *vice versa*. The plutonium spectra obtained for samples were generally less precise than those recorded for the earlier work[1], the mean coefficient of variation for scans being 1.13% compared with the previous value of 0.74%. This appeared to be due to a loss in sensitivity arising from a small H.T. leakage between the ion source block and the focus plates.

Results and discussion

Determination of the isotopic mass percentage of ^{239}Pu

Eqn. (3) involves the terms "mass percentage of ^{239}Pu" and "mass percentage of ^{238}U". These could be determined by a mass analysis for an aliquot of sample taken directly without addition of tracer, but in the interests of minimising the number of mass analyses it is worth examining the additional error that would be introduced by making these determinations in the presence of the tracer.

The ^{242}Pu tracer had the following isotopic composition: ^{238}Pu 0.3%, ^{239}Pu 0.4%, ^{240}Pu 0.5%, ^{241}Pu 0.2%, ^{242}Pu 98.4%, ^{244}Pu 0.2%. Thus in addition to determinations of ^{239}Pu, the main isotope in the samples, it should be possible to determine small quantities of ^{240}Pu and ^{241}Pu for samples which may be assumed to contain no ^{242}Pu. This assumption was justified in the present case for the two samples used contained $\gtrsim$0.01% ^{242}Pu. If isotopic ratios for sample, tracer, and mixture of sample and tracer are denoted by S, T, and M respectively, then $S_{240/239}$ and $S_{241/239}$ may be found using the following expressions:

$$S_{240/239} = \frac{M_{240/242} - T_{240/242}}{M_{239/242} - T_{239/242}} \tag{5}$$

$$S_{241/239} = \frac{M_{241/242} - T_{241/242}}{M_{239/242} - T_{239/242}} \tag{6}$$

These ratios may then be used to calculate the isotopic mass percentage of ^{239}Pu. Values found in this way for two samples are listed in Table I.

TABLE I

MASS PERCENTAGES OF ^{239}Pu DETERMINED IN PRESENCE OF ^{242}Pu TRACER

	Isotopic mass percentage of ^{239}Pu	
	sample A	*sample B*
Determinations	96.04	95.89
	95.71	96.02
	95.94	95.96
	95.98	95.93
	95.94	95.86
	96.02	95.93
Mean value and standard deviation	95.94 ± 0.12	95.93 ± 0.06
Comparison value	$95.95_2 \pm 0.01_0$	$95.97_7 \pm 0.01_3$

The comparison values were determined using aliquots of "unspiked" sample and these show that the results obtained from mixture analyses contain no serious systematic error.

The precision of a mass percentage determination made in the presence of the tracer is 5–10 times worse than that of a direct determination, but this should still be adequate for the present purposes. Thus in the work described previously[1] the mean precision found for an isotopic dilution determination of the concentration of ^{239}Pu was 0.20%. If a separate mass spectrometric analysis is made to find the isotopic composition of the plutonium sample, then the mass percentage of ^{239}Pu is determined to ~0.01%, so the precision of a determination of total plutonium is also 0.20%. If, instead of making separate determinations of the concentration of ^{239}Pu and of the isotopic composition of the plutonium sample, the whole of this information is obtained from a single mass analysis then, accepting the data in Table I as typical, the precision of a determination of total plutonium will become 0.22%*. Thus in considering the isotopic dilution method for routine determinations of plutonium, it seems that little would be lost by basing determinations on a single mass analysis, for the overall error is increased only from 0.20% to 0.22%, whereas there would be a considerable saving in the mass spectrometric effort required.

The above account omits consideration of the isotope ^{238}Pu. The determination of small quantities of this isotope in samples of the type considered here is subject to interference by ^{238}U. This criticism applies to a result obtained from an "unspiked isotopic analysis" as well as to a mixture analysis so it is probably simpler to make the determination by α-spectrometry.

It may be concluded that a determination of the concentration of total plutonium could be made by a single mass spectrometric analysis with little loss in precision for samples of the present type where the ^{242}Pu content is negligible. However, in considering the application of the method to solutions of dissolved fuel elements it would be necessary to consider the growth of ^{242}Pu with increasing irradiation time. Using

* This value (0.22%) is obtained by compounding the errors 0.20% for the determination of the concentration of ^{239}Pu and ~0.1% for the determination of the isotopic mass percentage of ^{239}Pu. However, when these determinations are based on the same mass analysis the two errors are not completely independent, and the overall error will be slightly smaller (0.21_2%). This point is discussed in Appendix 1.

published data for the variation of plutonium isotopic composition with irradiation in graphite[10,11] and in heavy water[12,13] moderated reactors it may be shown that the ^{242}Pu correction will be very small for irradiations of ~1000 MWD/tonne, and that if necessary the method could be extended to 5–6000 MWD/tonne by calculating corrections. This point is considered in Appendix 2.

Determination of the isotopic mass percentage of ^{238}U

In a similar way the isotopic composition of the uranium in the sample could be obtained from a mixture analysis by correction for the presence of the various tracer isotopes. The isotopic composition of the tracer was as follows: ^{233}U 99.8%, ^{234}U 0.17%, ^{235}U 0.004%, ^{238}U 0.02%. Assuming natural uranium is used as the charge material for the fuel elements, the initial isotopic composition of the sample would be ^{234}U 0.005%, ^{235}U 0.72%, ^{238}U 99.27%. In the course of irradiation the abundance of ^{235}U would decrease and a small quantity of ^{236}U would be produced; these isotopes could be measured in the presence of the tracer. It would be difficult to determine the abundance of ^{234}U, but as it is only present to the extent of 0.005%, changes in its concentration are not likely to be significant. Table II records values found for the isotopic mass percentage of ^{238}U in two samples, and again, in each case, one comparison value obtained using an aliquot of "unspiked sample". As the abundances of ^{234}U and ^{236}U were very small, these isotopes were not determined, so the values listed in the Table are based only on the measurement of either $^{235}U/^{233}U$ and $^{238}U/^{233}U$ ratios, or $^{235}U/^{238}U$ ratios.

TABLE II

MASS PERCENTAGES OF ^{238}U DETERMINED IN PRESENCE OF ^{233}U TRACER

	Isotopic mass percentage of ^{238}U	
	sample A	*sample B*
Determinations	99.32	99.28
	99.28	99.31
	99.32	99.32
	99.34	99.32
	99.32	99.31
	99.31	99.32
Mean value and standard deviation	99.32 ± 0.02	99.31 ± 0.02
Comparison value	$99.32_4 \pm 0.00_2$	$99.32_6 \pm 0.00_2$

Again the precision of a single determination is ~10 times worse than that achieved by a careful analysis of an "unspiked sample", but even so the random error of 0.02% is insignificant for the present purposes.

Calibration of the mixed ^{242}Pu–^{233}U tracer

Eqn. (3) also includes the term $[^{242}Pu]_t/[^{233}U)_t$. This concentration ratio for the tracer is determined by an isotopic dilution calibration in which aliquots of tracer are mixed with aliquots of a mixed uranium–plutonium standard. Apart from the mass spectrometric determinations the only sources of random error are those involved in preparing the uranium–plutonium standard. Once weighed quantities of

plutonium and uranium have been mixed, subsequent dilutions do not alter the [Pu]/[U] ratio, so in principle errors associated with the use of standard flasks and pipettes are eliminated. In practice, in view of the large concentration ratio, a plutonium metal standard is weighed, dissolved, and a suitable aliquot added to a flask containing a weighed quantity of U_3O_8, but the overall error for this stage can be made quite small. The mixed standard is then diluted to give a plutonium concentration of ~0.1 μg/g, and aliquots mixed with aliquots of the tracer. The results of the calibration are recorded in Table III.

TABLE III

CALIBRATION OF $^{242}Pu/^{233}U$ TRACER

$\frac{[^{242}Pu]_t}{[^{233}U]_t}$	*Mean value and standard deviation*
0.0003080	
0.0003087	
0.0003087	0.0003088 ± 0.0000005
0.0003090	
0.0003093	(C.O.V. 0.17%)
0.0003094	

The precision (1 standard error) for the mean value of the mass spectrometric determination of the $[^{242}Pu]_t/[^{233}U]_t$ ratio is thus 0.07%. If this is combined with errors arising from the determinations of the isotopic mass percentages of ^{239}Pu and ^{238}U (made in this case for a separate aliquot of standard) and dilution errors, the overall calibration error becomes 0.08%. It should be noted that this value does not include errors arising from uncertainties in such factors as stoichiometry of U_3O_8, etc.

Determination of the [Pu]/[U] ratio for samples

The mixed tracer was used to determine the [total Pu]$_s$/[total U]$_s$ concentration ratio for two samples. For each determination measurements were made of the $M_{239/242}$, $M_{240/242}$, $M_{241/242}$, $M_{238/233}$, and $M_{235/233}$ mixture ratios in a single mass analysis and used with the following equation:

$$\frac{[Pu]_s}{[U]_s} = \frac{[^{242}Pu]_t}{[^{233}U]_t} \cdot \frac{233}{242} \cdot \frac{239(M_{239/242} - T_{239/242}) + 240(M_{240/242} - T_{240/242}) + 241(M_{241/242} - T_{241/242})}{238(M_{238/233} - T_{238/233}) + 235(M_{235/233} - T_{235/233})} \quad (7)$$

Results obtained in this way are recorded in Table IV.

The values found for the precision of a single determination of the [Pu]/[U] ratio are 0.31% and 0.22% for the two sets of results respectively, giving a mean value of 0.27%; allowing for uncertainties in the calibration of the tracer gives an overall mean precision of 0.28%. The last column of Table IV records the coefficient of variation calculated for each result from the observed random errors in the various isotopic ratios measured for the mixture. It is clear that these precision measures are consistent with the observed variation of the results for the [Pu]/[U] ratio, and that if the method were to be used on a routine basis in a chemical plant, they could

provide a means of control over analyses. This point has been discussed in detail elsewhere for plutonium determinations[1].

Thus the isotopic dilution method may be used to determine the [Pu]/[U] concentration ratio for a solution containing both of these elements; the precision (1σ) is ~0.3% for a result based on a single mass spectrometric analysis.

TABLE IV

RESULTS FOR [Pu]/[U] RATIO DETERMINATIONS

Sample	$\frac{[\text{total Pu}]}{[\text{total U}]}$	*Mean value and standard deviation*	*Precision calculated from mass analysis* %
	0.0004120		0.14
	0.0004120		0.17
A	0.0004122		0.12
	0.0004126		0.19
	0.0004127		0.35
	0.0004154		0.41
		0.0004128 ± 0.0000013 (C.O.V. 0.31%)	
	0.0004072		0.19
	0.0004075		0.19
B	0.0004076		0.25
	0.0004083		0.14
	0.0004086		0.14
	0.0004096		0.17
		0.0004081 ± 0.0000009 (C.O.V. 0.22%)	

Corrections required in the calculation of the quantity of uranium present in a given mass of fuel elements

The total quantity of plutonium present in a solution of dissolved fuel elements will be given by the product of the measured [Pu]/[U] ratio and the total quantity of uranium present, so in addition to the random error of 0.3% noted above the final result for the quantity of plutonium will also involve uncertainties in relating the quantity of uranium to the mass of fuel elements; thus corrections will be required for loss of uranium both by fission and by conversion to plutonium. In the interests of making a complete investigation the preceding account has been based on the determination of the concentration of total uranium, and corrections for the quantity of ^{235}U transmuted and ^{236}U produced could be calculated from the uranium mass spectrum. However, it would in fact be simpler to omit consideration of these isotopes (and ^{234}U) in the calculation of both the concentration ratio and the mass of uranium, for then the only correction required will be for loss of ^{238}U during the irradiation. Deletion of the term ($M_{235/233} - T_{235/233}$) from eqn. (7) will give a determination of the [Pu]/[^{238}U] concentration ratio. The quantity of ^{238}U present in a batch of irradiated fuel elements will be given by the product of the mass of fuel elements and the original isotopic mass percentage of ^{238}U provided a correction is made for the loss of ^{238}U (mainly by conversion to plutonium). This correction may be calculated from the measured [Pu]/[^{238}U] ratio, and at low irradiations it will be small and the uncertainty negligible. At higher irradiations further corrections would be required

for plutonium consumed by fission, but presumably these could also be calculated from the measured values of the [Pu]/[^{238}U] ratio and the plutonium isotopic composition.

Possible application to accounting analyses in chemical processing plants

The procedure described appears to have many advantages if considered as a possible means of accountancy control in a chemical processing plant. For a solution containing a known mass of fuel elements a determination could take the following form. An aliquot of plant solution would be mixed with an aliquot of tracer. Neither aliquot need be measured accurately, for it is sufficient merely to ensure that the quantities mixed provide suitable $M_{239/242}$ and $M_{238/233}$ ratios for precise measurement in a mass spectrometer; an accuracy of say 20–30% would be adequate for each aliquot. Once mixed the method does not require a quantitative separation of either uranium or plutonium, for it is only necessary to ensure that the final specimens should contain sufficient material for a satisfactory mass spectral analysis. Thus a yield of 1–2% is adequate for uranium, and a minimum of perhaps 50% for plutonium. Under these conditions a single mass spectrometric analysis should provide a determination of the total plutonium content of the solution with a precision (1σ) of ~0.3% together with uncertainties in the total quantity of uranium calculated from the mass of fuel elements.

In practice it would seem preferable to make dilutions and to take aliquots as accurately as possible. A single mass spectrometric analysis could then provide information for the following purposes: (*1*) a determination of the [Pu]/[U] concentration ratio independent of plant sampling errors, (*2*) determinations of both plutonium and uranium concentrations with high analytical precision but also including sampling errors, (*3*) a determination of the plutonium isotopic composition from which the specific activity could be calculated with sufficient precision for radiochemical determinations.

At the present stage of development of mass spectrometers the method described would probably be too time-consuming to be applied at *frequent* intervals to a chemical plant. However, even in its present form it could provide a valuable supplement to existing methods. For example, one method of plant control is based on frequent radiochemical determinations of plutonium. These also require a knowledge of the specific activity of the plutonium, but this may be determined at less frequent intervals to give an average correction factor, either by a direct determination of the activity/mass ratio for the pure product, or by making a mass spectrometric analysis for a "bulked sample" of feed solution. In the latter case much would be gained by replacing this simple isotopic analysis by the procedure described in the present paper, for this would still provide the required specific activity determination, and in addition would give an independent and precise analysis for accountancy control. Sampling errors would be involved in preparing a "bulked aliquot", but for a plant operated on a batch basis this error would be small if the [Pu]/[U] ratio did not vary greatly from batch to batch. Additional uncertainties may be introduced in a plant operated on a continuous basis, but errors associated with proportional sampling devices are outside the scope of this paper.

DETERMINATION OF ^{235}U IN ENRICHED URANIUM FUEL ELEMENTS

In view of the apparent advantages of employing a ratio technique for the determi-

nation of plutonium in natural uranium fuel elements, it is natural to enquire whether a similar procedure could be applied to the determination of ^{235}U in highly enriched uranium fuel elements. In this case there is no experimental work to present so only a brief discussion will be given.

The problem may be considered in terms of the Dounreay Materials Testing Reactor chemical plant[5]. This is designed to process fuel elements of enriched uranium (93% ^{235}U)–aluminium alloy which have been irradiated to an extent that 20% of the ^{235}U originally present has been consumed by fission or by neutron capture. The requirements for plant accounting analyses are (*1*) a determination of the ^{235}U content of the irradiated fuel elements to provide a "plant input figure" of fissile material, (*2*) a determination of the quantity of ^{235}U consumed in the reactor for costing purposes.

A previous paper assessed the precision of the isotopic dilution method for the determination of ^{235}U, and indicated a value of $\sim$0.3% (1σ) for a single determination made for an aliquot of dilute mock feed solution[2]. For a reactor of the Dido type a charge of fuel elements contains $\sim$2,500 g of ^{235}U[14], and this might be processed in a chemical plant in ten batches, each containing 250 g[5]. Thus to determine the quantity of ^{235}U remaining in a charge of fuel elements either an aliquot must be taken from each batch and these combined to give a solution representative of the charge, or a determination made for each batch. The precision of a single determination made for the solution of combined aliquots would be $\sim$0.3%, and the overall precision obtained by making a single analysis for each of the ten batches would be $\sim$0.1%. The quantity of ^{235}U consumed in the reactor is then obtained by difference between the above quantity and that known to be present in a charge before irradiation, so the corresponding errors will be 1.2% and 0.4% respectively.

The above precision values refer only to the mass spectrometric method, and do not include plant sampling errors. The latter could well be considerably larger than the mass spectrometric error, and so will be especially significant in the determination of the quantity of ^{235}U consumed. However, in principle at least, these could be eliminated by a ratio procedure involving determinations of ^{235}U and a suitable fission product. The use of a radioactive fission product to determine the quantity of ^{235}U consumed may not be acceptable, for corrections will be required for its decay and an accurate knowledge of the reactor irradiation time and subsequent "cooling" time may not be available. However, this criticism would not apply to the use of a stable fission product provided the precursors are of short half-life.

Assuming that an acceptable stable fission product nuclide (denoted by ^{j}F) can be chosen, a ratio procedure could take the following form.

The concentration of ^{235}U in a plant solution may be obtained using eqn. (8) where $R(U)$ represents a function of the isotopic ratios determined by mass spectrometry for uranium; definitions of other symbols used are analogous to those used for eqn. (1).

$$[^{235}U]_s = [^{233}U]_t \cdot \frac{\text{mass tracer aliquot}}{\text{mass sample aliquot}} \cdot R(U) \cdot \frac{235}{233} \cdot D \qquad (8)$$

Similarly the concentration of the selected fission product nuclide ^{j}F may be determined by mixing it with an aliquot of a tracer enriched in isotope i:

$$[^jF]_s = [^iF]_t \cdot \frac{\text{mass tracer aliquot}}{\text{mass sample aliquot}} \cdot R(\text{F.P.}) \cdot \frac{W_j}{W_i} \cdot D \qquad (9)$$

where R(F.P.) represents a function of the various isotopic ratios determined for the fission product element; W_j and W_i are the atomic weights of isotopes j and i. Combining eqns. (8) and (9) gives:

$$\frac{[^jF]_s}{[^{235}U]_s} = C \cdot \frac{R(\text{F.P.})}{R(U)} \qquad (10)$$

where C is the product of a numerical constant and a concentration ratio determined for the tracer by calibration. Eqn. (10) is analogous to eqn. (3) and does not involve a knowledge of the mass of aliquots of sample or tracer, or of dilution factors. If a symbol k is now used to define the ratio of the number of atoms of ^{235}U destroyed, both by fission and by neutron capture, to the number of atoms of the selected fission product nuclide produced, eqn. (10) may be modified to give:

$$\frac{U_c}{U_r} = \frac{k.C.\ R(\text{F.P.})}{R(U)} \qquad (11)$$

where U_c is the quantity of ^{235}U consumed in the reactor, and U_r is the quantity remaining after irradiation. In practice small corrections will be required for the quantity of ^{235}U produced from ^{234}U, and for fission products derived from ^{238}U and ^{239}Pu. If the quantity of ^{235}U in a charge of fuel elements before irradiation is denoted by U_I, U_r and U_c may then be obtained as follows:

$$U_r = U_I \cdot \frac{1}{1 + k.C.\dfrac{R(\text{F.P.})}{R(U)}} \qquad (12)$$

$$U_c = U_I \cdot \frac{k.C.\dfrac{R(\text{F.P.})}{R(U)}}{1 + k.C.\dfrac{R(\text{F.P.})}{R(U)}} \qquad (13)$$

In eqns. (12) and (13) the effect of uncertainties in the determination of plant solution volumes, dilution factors, etc., is completely eliminated, but unless the quantity of ^{235}U originally present in each batch is known and "plant hold-up" is negligible, this would be strictly true only if a complete charge of fuel elements could be dissolved altogether and a single representative sample taken. In practice volume and dilution data will be involved either in the preparation of a bulked sample typical of the ten batches, or in the calculation of the overall R(F.P.)/R(U) ratio from ten individual determinations, but unless the [selected fission product]/[^{235}U] ratio varies widely between batches, the uncertainty introduced by plant sampling errors in this way will be small.

If the ^{235}U usage is of the order of 20%, the expression $k.C.\ R$(F.P.)/R(U) will have a value of $\sim$0.25, so if the percentage error in this expression is x the corresponding errors introduced into U_r and U_c will be 0.2 x and 0.8 x respectively. Thus, compared

with the direct determinations outlined earlier, in the ratio procedure the significance of experimental errors is reduced by a factor of 5 both for the determination of the quantity consumed and for the determination of the plant input figure.

In eqns. (12) and (13) the term C is obtained by a mass spectrometric calibration of the mixed tracer, so uncertainties are introduced only by the random errors in the isotopic analyses and by those in the preparation of a mixed standard of ^{235}U and the natural element form of the fission product; the term $R(F.P.)/R(U)$ involves only isotopic ratios determined by mass spectrometry. These quantities are analogous to the first two terms of eqn. (3), and under favourable conditions a precision approaching that of the $[Pu]_s[U]_s$ ratio determinations should be achieved. An additional uncertainty, however, is introduced by the term k relating the number of ^{235}U atoms destroyed to the number of atoms of the chosen fission product nuclide, for there is both the random error in the determination of k, and the question of whether it varies with irradiation conditions, etc. This, in fact, is the quantity controlling the feasibility or otherwise of the method. The following is not intended to be a complete discussion of this problem, but it is clear that the fission product nuclide selected must at least satisfy the following conditions: (*a*) the variation of k with neutron energy should be a minimum, (*b*) its neutron cross section should be small, (*c*) its precursors should have short half-lives, (*d*) there should be no segregation of the fission product element from uranium in the dissolver tank of the chemical plant, (*e*) subsequently the separation of the fission product element from uranium in the chemical plant should be sufficient to prevent errors arising from the use of recycled material, and (*f*) the element should be amenable to a mass spectrometric analysis, and a suitable tracer should be available.

It is likely that no one fission product element will be wholly satisfactory. However, the basis of a determination need not be restricted to one element, for by using both side filaments in the ion source it is quite feasible to determine both uranium and several fission products[15] in a single mass spectrometric analysis. A determination could then take the following form. It would be based primarily on the accurate determination of a fission product chosen for minimum variation of k with neutron spectrum. For a given fission product element probably more than one isotope could be used independently, and for preference the determination would be based on two elements chosen to be close to each of the peaks of the thermal fission yield/mass number curve. If the variation of k between charges of fuel elements is found to be significant, then given a precise determination of a fission product for which k varies over a relatively small range, the selection of the appropriate value of k might be based on the determination of the relative quantity of a third fission product element having the maximum variation of k with neutron spectrum, chosen, for example, to be close to the minimum of the thermal fission yield/mass number curve. In this way several independent values of $R(F.P.)/R(U)$ and the appropriate value of k might be obtained through a single mass spectrometric analysis.

One difficulty in the proposed scheme is that the quantity of feed solution requiring treatment would be much greater than that involved in a direct determination of ^{235}U. A direct determination requiring $\sim 2\ \mu g$ ^{235}U involves only ~ 0.4 mC of fission product activity, whereas a portion of solution containing $\sim 1\ \mu g$ of an element on either maximum of the fission yield curve would contain ~ 40 mC of activity, so handling problems would be rather more severe. The concentration of a fission product

nuclide in the minimum of the fission yield curve would be lower by a factor of the order of 100, so in this case the choice of element is essentially restricted to one having a high sensitivity in a mass spectrometer. ^{115}In is a possibility; it has the disadvantage of a long-lived precursor (^{115}Cd, 43 d), but the yield of this is much lower than that of its shorter lived isomer (^{115}Cd, 54 h)[16], so this uncertainty might be acceptable in the calculation of a correction.

Given a suitable fission product, or combination of fission products, a single mass spectrometric analysis could provide information for the following purposes: (*1*) a determination of the quantity of ^{235}U consumed in the reactor; this would be nearly independent of plant sampling errors, and the effect of random errors in the mass spectrometric analyses would be diminished by a factor of 1.25; (*2*) a determination of the ^{235}U input to a chemical plant; again this would be nearly independent of sampling errors, and the significance of random errors in the mass analyses reduced by a factor of 5; (*3*) a determination of the ^{235}U concentration in the plant feed solution but including sampling errors; (*4*) an isotopic analysis of the plant uranium (by correction for the presence of the various tracer isotopes) to provide the mass percentage of ^{235}U and the equivalent weight of the uranium for use with other analytical methods.

CONCLUSIONS

The use of a ratio procedure for the analyses of feed solutions made in chemical processing plants for accountancy purposes offers several powerful advantages. Thus plant sampling errors are nearly eliminated and this enables high precision techniques to be exploited. The data presented show that for solutions of natural uranium fuel elements the [Pu]/[U] ratio could be determined with a precision (1σ) of $\sim$0.3% by a single mass spectrometric analysis. The samples used in this work contained $>$0.01% ^{242}Pu; in practice the ^{242}Pu content would increase with irradiation time, but it can be shown that the ^{242}Pu correction will usually be very small for an irradiation of $\sim$1000 MWD/tonne, and that by calculating this correction it should be possible to extend the method to solutions obtained even after irradiations of 5–6,000 MWD/tonne.

In principle a similar procedure might be applied in a chemical plant processing fuel elements containing highly enriched ^{235}U. In this case both the quantity consumed in the reactor and the input figure for the chemical plant would be related to a [stable fission product]/[^{235}U] ratio. The method is less fundamental than a direct determination of ^{235}U and includes the uncertainty in the variation of the ratio (atoms ^{235}U destroyed)/(atoms fission product nuclide produced) with neutron spectrum, but this disadvantage might be outweighed by the near elimination of plant sampling errors, and the five-fold reduction in significance of instrumental errors in the determination of both of the required quantities.

The chief limitation of the mass spectrometric procedure is the time-factor. The [Pu]/[U] ratio determinations were made at the rate of only one per day. This could be raised to two per day, but considerable time is also required for the actual measurement of the various ratios after they have been recorded, for each complete mass spectrometric analysis involved over 100 estimates of isotopic ratios. The method could obviously be made even more attractive by instrumental developments permitting mass spectra to be both recorded and measured more rapidly.

APPENDIX I

ERRORS INVOLVED IN THE CALCULATION OF THE CONCENTRATION OF TOTAL PLUTONIUM FROM A SINGLE MASS SPECTROMETRIC ANALYSIS

The expression for the concentration of total plutonium (eqn. 1) includes the following term:

$$\frac{M_{239/242} - T_{239/242}}{(\text{mass percentage } ^{239}\text{Pu})_s} \tag{14}$$

or expressing "mass percentage" in terms of the ratios $S_{240/239}$ and $S_{241/239}$:

$$(M_{239/242} - T_{239/242}) \left(1 + \frac{240}{239} S_{240/239} + \frac{241}{239} S_{241/239}\right) \tag{15}$$

Expression (15) will apply directly when the determinations of $M_{239/242}$ and the isotopic composition of the sample are independent (*i.e.* based on separate mass spectrometric analyses). When these two quantities are determined by the same mass analysis the ratios $S_{240/239}$ and $S_{241/239}$ are not measured directly, but are calculated from the observed mixture and tracer ratios, so the precision for the determination of these two terms will usually be worse than that obtained by a direct analysis. Thus the *apparent* increase in error when a determination of the concentration of total plutonium is based on a single mass spectrometric analysis, instead of on separate analyses for $M_{239/242}$ and the isotopic composition, will arise from the increase in the error due to the second part of expression (15). Typical values of the ratios and of coefficients of variation for direct determinations and for values calculated from mixture analyses respectively are: $S_{240/239}$, 0.040 (0.25%, 2%); $S_{241/239}$, 0.0024 (1%, 15%); the corresponding errors for the second part of expression (15) are then 0.01% and 0.09%.

In basing a determination of the concentration of total plutonium on a single mass spectrometric analysis the error component arising from the determination of the isotopes ^{240}Pu and ^{241}Pu will therefore increase, but in fact this will be offset to some extent by a small decrease in the significance of the error in the measurement of the ratio $M_{239/242}$. Thus if eqns. (5) and (6) are used to express $S_{240/239}$ and $S_{241/239}$ solely in terms of mixture and tracer ratios, expression (15) becomes:

$$(M_{239/242} - T_{239/242}) + \frac{240}{239}(M_{240/242} - T_{240/242}) + \frac{241}{239}(M_{241/242} - T_{241/242}) \tag{16}$$

Then if the percentage error in $M_{239/242}$ is $\triangle M$, the errors introduced by this into expressions (15) and (16) will be

$$\frac{M_{239/242}}{M_{239/242} - T_{239/242}} \cdot \triangle M \tag{17}$$

and

$$\frac{M_{239/242}}{(M_{239/242} - T_{239/242}) + \frac{240}{239}(M_{240/242} - T_{240/242}) + \frac{241}{239}(M_{241/242} - T_{241/242})} \cdot \triangle M \tag{18}$$

respectively. Typical values of the various ratios are $M_{239/242}$, 1; $M_{240/242}$, 0.045; $M_{241/242}$, 0.005; $T_{239/242}$, 0.005; $T_{240/242}$, 0.005; $T_{241/242}$, 0.002$_3$; substituting these gives a value of 0.96 for the ratio of expression (18) to expression (17).

Assuming a value of 0.20% for the coefficient of variation for the factor ($M_{239/242} - T_{239/242}$), then when the ratio $M_{239/242}$ and the isotopic composition of the plutonium are determined by separate mass spectrometric analyses, the errors to be combined are 0.20% and 0.01%, and the coefficient of variation for expression 15 is 0.20$_0$%. When the two quantities are determined by a single mass spectrometric analysis the errors to be combined are 0.96 × 0.20% and 0.09%, so the overall error for expression (16) is 0.21$_2$%. (For comparison a direct combination of errors of magnitude 0.20% and 0.09% would give an overall value of 0.21$_9$%).

The above account is incomplete for the error in the factor ($M_{239/242} - T_{239/242}$) will usually be less than 0.20%, and some other error components (calibration of tracer, uncertainty in mass of aliquots of sample and tracer, etc.) will be common to both types of determination. However, it illustrates that relatively little should be lost in basing a determination on a single mass spectrometric analysis. For material produced after longer irradiations, the relative quantities of ^{240}Pu and ^{241}Pu will be larger. The disparity between the two methods of estimating ^{240}Pu and ^{241}Pu should then decrease, and further the value of the coefficient of $\triangle M$ in expression (18) will also decrease. Thus the single analysis method should continue to be attractive until the growth of ^{242}Pu becomes the limiting factor.

APPENDIX 2

GROWTH OF ^{242}Pu WITH IRRADIATION TIME

The procedure described in "Determination of plutonium in natural uranium fuel elements" involves the assumption that the ^{242}Pu content of the samples is negligible. This may be acceptable for uranium irradiated to the extent of perhaps 1,000 MWD/tonne, but at higher irradiations the ^{242}Pu content will increase and will require consideration. However, even when the ^{242}Pu content is significant, if it is small it may still be possible to make a determination by one mass spectral analysis. For a given reactor and operating procedure the variation of plutonium isotopic composition with irradiation might be found either by calculation or by experiment. Using these data curves may be constructed showing the variation of the ^{242}Pu/^{239}Pu ratio with both the ^{240}Pu/^{239}Pu ratio and the ^{241}Pu/^{239}Pu ratio. For any given sample the measured ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu ratios (*i.e.* calculated from measured mixture and tracer ratios) may each be used with the curves to find the appropriate ^{242}Pu/^{239}Pu ratio, which is then used in the calculation of the total quantity of plutonium. In order to illustrate the errors introduced by such a procedure the data quoted for a typical natural uranium graphite moderated power reactor have been taken as an example of the variation of plutonium isotopic composition[11], and used in the calculations below. In practice, for a given reactor operated at a fairly constant irradiation level, calibration curves might be constructed from a few "unspiked isotopic analyses" for the plant solutions.

Eqns. (5) and (6) enable the $S_{240/239}$ and $S_{241/239}$ ratios to be calculated from mixture and tracer ratios when the sample contains a negligible quantity of ^{242}Pu. If, however, the ratio $S_{242/239}$ has a finite value, the equations take the following modified form:

$$S_{240/239} = \frac{M_{240/242} - T_{240/242}}{M_{239/242} - T_{239/242}} + \frac{M_{239/242} \cdot T_{240/242} - M_{240/242} \cdot T_{239/242}}{M_{239/242} - T_{239/242}} \cdot S_{242/239} \quad (19)$$

$$S_{241/239} = \frac{M_{241/242} - T_{241/242}}{M_{239/242} - T_{239/242}} + \frac{M_{239/242} \cdot T_{241/242} - M_{241/242} \cdot T_{239/242}}{M_{239/242} - T_{239/242}} \cdot S_{242/239} \quad (20)$$

Eqn. (1) also becomes:

$$[\mathrm{Pu}]_s = [^{242}\mathrm{Pu}]_t \cdot \frac{\text{mass tracer aliquot}}{\text{mass sample aliquot}} \cdot \frac{D}{242} \cdot \frac{M_{239/242} - T_{239/242}}{1 - M_{239/242} \cdot S_{242/239}} \cdot (239 + 240\, S_{240/239} + 241\, S_{241/239} + 242\, S_{242/239}) \quad (21)$$

Eqn. (19) may be considered in two parts: the first term which is analogous to eqn. (5), and a second term involving $S_{242/239}$, the $^{242}Pu/^{239}Pu$ ratio for the sample. Assuming a value of unity for the $M_{239/242}$ ratio throughout, the relative values of these terms may be calculated for various irradiation levels. In this way it may be shown that the contribution of the second term is very small, both for $S_{240/239}$ and $S_{241/239}$, increasing from ~0.01% at 2,000 MWD/tonne to ~0.05% at 8,000 MWD/tonne. Thus the errors introduced in applying these corrections will be negligible, and it is justified to use the calculated values of $S_{240/239}$ and $S_{241/239}$ to find $S_{242/239}$.

By using the calibration plots (based in this case on reference[11]) the errors in the $^{242}Pu/^{239}Pu$ ratio corresponding to error values assumed for the $^{240}Pu/^{239}Pu$ and $^{241}Pu/^{239}Pu$ ratios may also be found, and then, using eqn. (21), the equivalent error for the total quantity of plutonium. This procedure has been used to calculate the values listed in Table V, where it has been assumed that $S_{240/239}$ and $S_{241/239}$ are determined to ± 0.0005 for values of 0.05 or less, and to 1% for values greater than 0.05, and also that a $M_{239/242}$ ratio of ~1 is used throughout.

TABLE V

ERRORS IN [Pu]$_s$ EQUIVALENT TO ERRORS IN $^{240}Pu/^{239}Pu$ AND $^{241}Pu/^{239}Pu$ RATIOS WHEN USED TO CALCULATE THE ^{242}Pu CORRECTION

Irradiation level MWD/tonne	*Error using $^{240}Pu/^{239}Pu$ ratio* %	*Error using $^{241}Pu/^{239}Pu$ ratio* %
2000	~0.01	~0.03
3000	0.04	0.02
4000	0.08	0.04
5000	0.13	0.07
6000	0.2	0.11
8000	0.5	0.2

The later entries in the second column are probably overestimates for as the $^{240}Pu/^{239}Pu$ ratio reaches 0.2–0.4 it will be determined with a better precision than 1%. It therefore seems that if necessary this interpolation procedure could be used, without introducing serious errors, up to an irradiation of 5–6,000 MWD/tonne. A similar calculation based on isotopic data for N.R.X.[12,13,17] combined with ^{242}Pu production rates calculated for M.T.R. Idaho[18] also gives results which are comparable (slightly smaller) with the errors listed in Table V.

SUMMARY

A procedure is described for the determination of the [total Pu]/[total U] concentration ratio for a given solution by an isotopic dilution method. Results obtained for two samples give a mean precision (1σ) of 0.3% for a determination made by a single mass spectrometric analysis. A possible application of the method would be its use for plutonium accounting analyses in a chemical plant processing natural uranium fuel elements, an important feature being the near elimination of the effect of plant sampling errors. An outline is also given of a similar procedure which might be used for the determination of ^{235}U in a plant processing enriched uranium–aluminium alloy reactor fuel.

RÉSUMÉ

Une méthode par dilution isotopique est décrite pour la détermination du rapport de concentrations [Pu total]/[U total] dans une solution donnée. Une application de ce procédé est possible dans les installations utilisant l'uranium naturel comme combustible.

ZUSAMMENFASSUNG

Beschreibung einer Isotopenverdünnungsmethode zur Bestimmung des Konzentrationsverhältnisses [total Pu]/[total U] in einer Lösung. Es wurde bei zwei Substanzproben durch eine Massenspektrometrische Analyse eine mittlere Präzision von 0.3% erzielt. Mögliche Anwendungen der Methode in uran-verarbeitenden Betrieben werden erwähnt.

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RADIOCHEMICAL SEPARATION OF COBALT*

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INTRODUCTION

The separation of cobalt-60 from other radio-isotopes emitting hard γ-rays is of great importance, *e.g.* in activation analysis**. In many irradiated samples (blood, steel, etc.) especially iron-59 and zinc-65 are present in large excess over the cobalt-60.

The methods suggested for the separation of cobalt-60 include paper chromatographic, ion-exchange, precipitation and extraction techniques[2–6]; but with a large excess of iron-59 or zinc-65 we found that none of these methods was quite satisfactory.

PŘIBIL *et al.*[7] made use of the extraordinary stability of the cobalt diethyldithiocarbamate complex for the selective colorimetric determination of microgram amounts of cobalt. The complex was extracted into chloroform and all other colored diethyldithiocarbamate complexes were decomposed by shaking with an aqueous solution of mercury(II).

The same reactions were applied by the present author for the radiometric determination of submicrogram amounts of cobalt, using either diethyldithiocarbamate-^{35}S or mercury-203 (in contradistinction to microgram amounts of cobalt, extraction with diethyldithiocarbamate at pH 14 was incomplete)[8].

In the present work cobalt and other carriers were added to the irradiated sample and extraction of the cobalt complex was carried out at pH 14. The treatment with mercury(II) was unnecessary, because iron-59 and zinc-65 were co-extracted only to the extents of 0.0005 and 0.04% respectively.

PROCEDURE

After the irradiation add metal-carriers in 100 μg*** amounts, ash and/or dissolve in mineral acid and, if necessary, separate the heavy metals by precipitation as the hydroxides.

Dissolve in a few ml of 1 *N* hydrochloric acid and place the solution in a tightly lidded P.V.C. pill-capsule of diameter 25 mm and height 76 mm.

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** KAISER AND MEINKE[1] carried out the neutron activation analysis of cobalt, using the *soft* γ-radiation of cobalt-60m ($t_{\frac{1}{2}}$ = 10.5 min).

*** Alternatively 1 mg of each metal is added as a carrier; in this case 0.05 *M* tartrate and 10 mg of diethyldithiocarbamate are used.

Dilute to 5 ml, add some phenolphthalein and add potassium sodium tartrate up to 0.01 *M**. Neutralise with alkali, add an excess of 0.6 ml of 10 *N* sodium hydroxide and then 1 mg of diethyldithiocarbamate*.

Shake mechanically** with 5 ml of carbon tetrachloride (AnalaR), centrifuge lightly to remove drops from the upper walls and remove the upper layer with a pipette. Rinse by shaking with alkaline tartrate, dry the carbon-tetrachloride layer by filtration (*e.g.* through a SS-595 paper) and evaporate by a stream of nitrogen to the volume of the well-type counter. Measure the radio-activity of cobalt-60 by scintillation counting*** and the amount of the cobalt complex with a spectrophotometer (4000 Å).

The time required for a determination in duplicate is 40 min; the efficiency for cobalt is about 50%.

DISCUSSION

The results (Table I) show that less than 0.0005 and 0.04% of iron and zinc respectively are extracted. About 0.05% of the activity of both pile- and cyclotron-produced

TABLE I

EXTRACTION OF IRON-59 AND ZINC-65 BY DIETHYLDITHIOCARBAMATE AT PH 14[a]

	^{59}Fe	*Pile*[b]	*Cyclotron*[c]
1	Freshly irradiated	40	48
2	After 70 days (1.5 times $T_{\frac{1}{2}}$)	105	185
3	As no. 2; purified[d]	<0.5	<3
4	As no. 2; no Co-carrier[e]	<0.5	<0.5
	^{65}Zn	*Pile*	
1	Non-purified	35	
2	Purified[f]	40	

[a] Tracer is added to give an original count-rate of 10^5 C/min; mean values of 4 experiments are given in C/min found in the final organic layer.

[b] ^{59}Fe was produced by the $^{58}Fe(n,\gamma)$ ^{59}Fe reaction; some ^{60}Co was formed (by (n,γ) reactions) from the small amounts of cobalt in the iron target. (Amersham – UK)

[c] ^{59}Fe was produced by the ^{59}Co (d, 2p)–^{59}Fe reaction (in concurrence with the ^{59}Co (d,p)–^{60}Co reaction) from a cobalt-target. Most of the ^{60}Co was removed by the manufacturer (Philips-Duphar, Amsterdam).

[d] Purified — after the addition of Fe- and Co-carriers — by N successive extractions with isopropylether from 7 *N* HCl, evaporation of the ether, addition of new carriers and HCl up to 7 *N*, and repetition (M-times) of the process. In column 2: N = 2 and M = 3, the efficiency for Fe and Co was 80 and 0.02% respectively In column 3: N = 3 and M = 2, and the respective efficiencies were 95 and 1%.

[e] Carrier-free cobalt is extracted very incompletely (see introduction).

[f] ^{65}Zn was purified by descending paper chromatography. The solvent (acetone–4 *N* HCl = 75 : 25) was allowed to drip off.

* Alternatively 1 mg of each metal is added as a carrier; in this case 0.05 *M* tartrate and 10 mg of diethyldithiocarbamate are used.

** Shaking was carried out in a vertical position in the "Microid flask shaker" at 900 periods per min for 3 min.

*** A Philips detector (PW 4111 W) and scaler (PW 4022-4032-4052), combined with an E.K.A.F. single channel analyser (30301–20102), were used.

iron-59 is due to cobalt-60. (For the pile-produced iron-59 the manufacturer gave the value: <0.1 %).

When the alkaline back-extraction is omitted or when it is replaced by a simple rinsing, results with iron-59 are 5 to 30 times higher. When the procedure is carried out with 1 ml of both layers, evaporation of the organic layer is not required but results with iron-59 are doubled.

Addition of the diethyldithiocarbamate reagent at lower pH values results in higher extraction percentages of iron-59. The addition of ammonium tartrate, sodium fluoride, pyrophosphate, "tiron", or ascorbic acid does not have any favourable influence on the results. The use of 10 mg of each carrier in the 5-ml volume resulted in precipitation. The addition of mercury(II) or potassium cyanide to the alkaline tartrate used for the back-extraction did not improve the results.

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SUMMARY

A method is described for the radiochemical separation of cobalt based on the extraordinary stability of cobalt diethyldithiocarbamate. Interferences are few; only very small amounts of zinc and iron accompany cobalt, which is important in neutron-activation analysis.

RÉSUMÉ

Une méthode est proposée pour la séparation radiochimique du cobalt, sous forme de diéthyldithiocarbamate; ce composé présente une stabilité remarquable.

ZUSAMMENFASSUNG

Es wird eine radiochemische Abtrennungsmethode für Kobalt beschrieben. Sie beruht auf der aussergewöhnlichen Stabilität des Kobalt–Diäthyl-dithiocarbamat Komplexes.

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SOME REMARKS ABOUT THE USE OF THE BOMB CALORIMETER

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For respiration experiments with cows, in which it is important to establish the energy balances, we had to determine the calorific value of many samples of feeding stuffs, faeces, urine, etc. These values were measured in a bomb calorimeter by determining the rise of temperature in the inner calorimeter vessel, keeping the water in the outer vessel at a constant temperature. For these experiments it is sufficient to attain an accuracy of 0.2–0.3%.

The experience obtained in this work gives rise to some remarks which may be useful to other workers in this field.

The accuracy of the thermometer

Usually in calorimetry a thermometer is used with a scale graduated to 0.01°, whilst readings are estimated to 0.001°. However, in verifying thermometers of this kind the accuracy is about 0.01° and certainly not 0.001° (private communication from Van der Waals Laboratory, Amsterdam). It is our opinion that, even in legally verified thermometers, both the initial and final temperature may be 0.005° in error, so that in unfavourable circumstances the maximum error will amount to about 0.01°. This means a relative error of about 0.5%, if the total temperature rise is about 2°. In the usual method of determining the combustion value this thermometer error undoubtedly provides the limiting factor.

In order to reduce the unfavourable influence of unknown thermometer errors our method was modified so that in all determinations nearly the same section of the thermometer could be used (see also COOPS *et al.*[1]). For our calorimetric determinations the initial temperature is always the same, being chosen as 19.0° (between 19.00 and 19.04). Furthermore so much material is burnt in the bomb that the temperature rise is between 1.6° and 1.9°. Thus, our end-temperatures are always between 20.6° and 20.9°. This range from 1.6° to 1.9° could be reduced if necessary; in fact nearly all temperature rises are between 1.7 and 1.8°. This method of measuring reduces considerably the influence of unknown thermometer errors. Since in calorimetric work the determinations are based on the known calorific value of substances such as benzoic acid, succinic acid, etc., it is not important to know the absolute temperature rise. As a matter of fact in our case thermometer errors from 19.0° to 20.6° are immaterial, so that it is enough to establish possible irregularities in the range 20.6°–

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20.9°; the irregularities over such a small interval will usually be negligible. Moreover, the section of the thermometer between 20.6 and 20.9 can be verified accurately with benzoic acid in the following manner. With different amounts of benzoic acid the water value of the calorimeter is determined. The amounts of benzoic acid are chosen so that the final temperatures are successively about 20.6, 20.7, 20.8 and 20.9°. If the water values corresponding to the different final temperatures are in good agreement, no thermometer corrections have to be applied. If the water values found over the range 20.6–20.9 do not agree sufficiently, a certain point in the region 20.6–20.9, for instance 20.6, is assumed to be correct and for the other points of the region such thermometer corrections are applied that the calculated water values correspond to the water value at the chosen point 20.6.

With a material such as benzoic acid (homogeneous and nonhygroscopic) the water value, if determined in duplicate, can be established with an accuracy of about 1 part in 1000 (0.1%). This means that in verifying the thermometer with benzoic acid as described, an accuracy can be obtained of 0.1% of the total rise (± 1.8°), *i.e.* about 0.002°.

In order to be able to start the measurements at the fixed temperature of 19°, we placed a simple electric heater (40 V, 50 Watt) in the inner calorimeter vessel. At the beginning of every determination the inner calorimeter vessel is filled with water, the temperature of which is somewhat less than 19°; the water is then warmed with the electric heater to nearly 19.0° and stirred for 10 min to ensure that equilibrium is established. In the outer vessel (water jacket) are placed an electric heater (220 V, 350 Watt) and a spiral copper tube for cooling with tap water. Mixing of the water in the outer vessel can simply be achieved by forcing air through the water with a rubber bulb. Thus the temperature of the outer vessel can also be adjusted at will, which is very important, for now one is always able to measure under standard conditions. The temperature of the outer vessel is chosen as about 0.5° lower than the expected final temperature in the inner vessel, thus, as a rule, the temperature in the outer vessel is 20.2° or 20.3°.

The measures mentioned above proved to ensure more reliable and more accurate results and, in our opinion, it would be desirable for calorimeters to be built so that the temperatures in the outer and inner vessels can be regulated.

A simple, accurate correction-formula

The temperature rise measured after the firing must be corrected because this rise is influenced by the differences between the temperatures of the inner and outer vessels. The best approximation of this correction is given by the theoretically derived formula of REGNAULT–PFAUNDLER[2], which can be written as follows:

$$c = \frac{V_1 - V_2}{R}\left(T_1 + T_2 + \ldots\ldots T_{n-1} + \frac{T_0 + T_n}{2} - n\,T_0\right) - n\,V_1$$

where V_1 and V_2 = temperature rise per time interval (30 sec) in the initial and final periods respectively, $T_0, T_1 \ldots T_n$ = temperature readings in the combustion period, R = temperature rise in the combustion period and n = number of time intervals (30 sec) in the combustion period.

The use of this formula involves a rather time-consuming calculation with every determination. However, for every calorimeter and bomb it is quite easy to derive

from the mentioned formula a very simple one, which is almost as accurate as the REGNAULT–PFAUNDLER formula. From a large number of observations it turned out that the temperature rise after the firing, if plotted graphically, always follows the same type of curve, practically independently of the kind of material burnt. The shape of the temperature–time curve is mainly determined by the material of the bomb and the construction of the apparatus. After the first time interval (30 sec) in the combustion period the rise is a certain fraction of the total rise ($T_1 = T_0 + \alpha_1 R$), and also after the second, third, etc. intervals ($T_2 = T_0 + \alpha_2 R$; $T_3 = T_0 + \alpha_3 R$; etc.). For the equation of REGNAULT–PFAUNDLER we now can write:

$$c = \frac{V_1 - V_2}{R} \left\{ n\,T_0 + (\alpha_1 + \alpha_2 + \ldots \alpha_{n-1} + \frac{\alpha_n}{2} (R - n\,T_0 \right\} - n\,V_1$$

or:

$$c = (V_1 - V_2)\,(\alpha_1 + \alpha_2 \ldots \alpha_{n-1} + \frac{\alpha_n}{2}) - n\,V_1$$

For our calorimeter and two old bombs (old-type bombs, manufacturer Julius Peters, Berlin) the combustion period is 5 min and we always use time intervals of 30 sec, therefore $n = 10$. For the calculation of $\alpha_1 + \alpha_2 + \ldots \alpha_{n-1} + \frac{1}{2}\alpha_n$ we used the readings of 48 determinations (hay, dried faeces, urine dried on cellulose, benzoic acid). The mean value of this sum proved to be 8.75 with a standard deviation of 0.06. Thus, for our calorimeter with old bombs the formula could be changed into:

$$c = (V_1 - V_2)\,8.75 - 10\,V_1 = -8.75\,V_2 - 1.25\,V_1$$

The algebraic signs of V must be carefully watched; a decrease of the temperature during the initial or the end period means that V is negative.

For our calorimeter with old bombs this very simple formula is nearly just as accurate as the original formula. The small fluctuations found for the sum $\alpha_1 + \alpha_2 +$ etc. (standard deviation 0.06) are mainly caused by the quick temperature rise in the first part of the combustion period, which entails inaccurate readings. These inaccurate readings also cause some uncertainty in using the formula of REGNAULT–PFAUNDLER.

For control the correction was calculated in both ways for 12 determinations. The results are given in Table I.

As can be seen, the differences between the pairs of corrections are negligible,

TABLE I

Organic matter	*I Simple formula*	*II Regnault–Pfaundler*	*I–II*
hay	−0.0042	−0.0042	0.0000
hay	−0.0021	−0.0021	0.0000
hay	−0.0011	−0.0009	−0.0002
hay	−0.0022	−0.0021	−0.0001
faeces	+0.0021	+0.0020	+0.0001
faeces	+0.0006	+0.0005	+0.0001
faeces	−0.0008	−0.0010	+0.0002
faeces	0.0000	−0.0001	+0.0001
flour	−0.0010	−0.0009	−0.0001
urine	−0.0004	−0.0003	−0.0001
urine	−0.0038	−0.0035	−0.0003
urine	−0.0031	−0.0030	−0.0001

especially if it is considered that the uncertainty in the readings and in the calibration of the thermometer is many times larger. For every calorimeter and bomb a corresponding simple formula can be derived after a number of determinations has been done. We found however that the difference between two bombs can be very large in this respect. The example given above holds for our two old bombs from Julius Peters, Berlin. For a newly received bomb (manufacturer also Julius Peters) it appeared that the heat exchange after the combustion was much slower than with the old bombs. Whilst the combustion period for the old bombs was only 5 min ($n = 10$), the combustion period for the new bomb appeared to be 9 min ($n = 18$). The correction formula for the new bomb proved to be: $c = -15.5\,V_2 - 2.5\,V_1$. The slow heat exchange of the new bomb can probably be attributed to a low heat conductivity of the material of the bomb and must be called an important disadvantage for two reasons: the determinations are more time-consuming and the calculation of the correction is less accurate. For calorimetric bombs material of high heat conductivity is to be preferred.

SUMMARY

In order to reduce the unfavourable influence of unknown thermometer errors, the method for the determination of the calorific value of organic matter in the calorimetric bomb is modified so that in all determinations nearly the same section of the thermometer is used. For the correction of the observed temperature rise a very simple formula is derived from the more elaborate formula of REGNAULT–PFAUNDLER.

RÉSUMÉ

L'auteur propose une modification de la détermination de la chaleur de combustion de substances organiques par la bombe calorimétrique, permettant d'éviter des erreurs dues au thermomètre. Pour la correction, on utilise une formule de REGNAULT–PFAUNDLER simplifiée.

ZUSAMMENFASSUNG

Beschreibung eines Verfahrens zur Eliminierung des Einflusses des Thermometerfehlers bei der Bestimmung des Kaloriengehaltes von organischem Material im Kalorimeter. Zur Korrektur wird eine vereinfachte Formel von REGNAULT–PFAUNDLER verwendet.

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DETERMINATION OF FORMIC ACID BY CATALYTIC OXIDATION WITH CERIUM(IV)

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Cerium(IV) has been used for the oxidative determination of organic compounds by several workers[1-4]. In most cases the oxidation proceeds to the formation of carbon dioxide, water, formic acid and higher fatty acids. Although it has been reported that formic acid is resistant to further oxidation, impurities present in the ceric salts may induce partial oxidation of formic acid; the reaction may thus be non-stoichiometric. This necessitates the use of empirical factors for the determination of certain compounds. In order to overcome this difficulty SHARMA AND MEHROTRA[2] suggested chromium sulphate as catalyst and a sulphuric acid concentration of 50–60%; formic acid is then oxidised by cerium(IV) to carbon dioxide. Other organic compounds which are normally oxidised to the formic acid stage by cerium(IV) are then also oxidised to the carbon dioxide stage and the reaction becomes more stoichiometric and better suited for quantitative work.

Under the conditions used by SHARMA AND MEHROTRA[2] there is always a danger of loss of volatile oxidation products .We therefore considered the possibility of using some catalyst in the presence of which formic acid can be oxidised at ordinary temperature. We have already described[4] a photochemical method for the oxidation of organic compounds at room temperature which eliminates the possibility of volatilisation of oxidation products.

Although SHARMA AND MEHROTRA did not discuss the mechanism of the catalytic action of chromic sulphate, it appears that chromium(III) is oxidised to the hexavalent state[5] which is re-reduced by formic acid. Among other oxidants used for the oxidation of formic acid, bromine reacts at ordinary temperatures[6], being reduced to hydrogen bromide. In presence of cerium(IV), bromine is regenerated and a chain reaction is set up which can be represented as follows:

$$2\ Br^- + 2\ Ce^{+4} \rightarrow Br_2 + 2\ Ce^{+3}$$

$$HCOOH + Br_2 \rightarrow 2\ HBr + CO_2$$

This reaction has been used as the basis for the oxidation of formic acid by cerium(IV) in the present investigation.

EXPERIMENTAL

Stock solutions of ceric salts were prepared by dissolving the requisite amount of ceric sulphate (A.R., B.D.H.) in sulphuric acid so that the final acidity was 1.0 *N*.

This solution was standardised iodimetrically[7] by running a blank as described below. Since formic acid may contain some oxidisable impurities it was distilled from a solution containing 100 ml of 90% formic acid, 2 g of ceric sulphate and 20 ml of 4 *N* sulphuric acid. In the distillate formic acid was determined by reduction of mercuric chloride; finally, the solution was diluted to give a concentration of 0.02 *M*.

Oxidation of formic acid

To a known amount of formic acid solution in an iodine flask, excess of cerium(IV) solution and 0.5–1.0 ml of 1% potassium bromide solution were added. The final solution was made 2 *N* in sulphuric acid. After about an hour, excess of 10% potassium iodide solution was added and the liberated iodine was titrated with standard sodium thiosulphate solution. A blank determination was run simultaneously on the same amounts of ceric sulphate and potassium bromide without formic acid. The difference between the test and blank runs corresponds to the equivalents of cerium(IV) consumed by the formic acid. Different amounts of formic acid and ceric sulphate solution were examined as indicated in Table I. The amount of potassium bromide was also varied; with insufficient concentrations of potassium bromide, the reaction time was longer while with high potassium bromide concentrations low results were obtained owing to loss of bromine. The results are given in the Table I.

TABLE I

Volume of 0.02 M formic acid (ml)	*Volume of 0.05 M cerium(IV) solution (ml)*	*Volume of 1% potassium bromide solution (ml)*	*Time for completion of the reaction (min)*	*Volume of 0.05 M cerium(IV) solution consumed (ml)*
1.0	2.0	0.5	45	0.80
2.0	3.0	0.5	60	1.64
5.0	4.0	1.0	80	3.98
10.0	6.0	1.0	100	3.95

Further oxidation of the photochemical oxidation products of certain hydroxy acids with cerium(IV)

The oxidation of malic, tartaric and citric acids were carried to the formic acid stage photochemically as described earlier[4]. To the oxidation products 1.0 ml of 1% potassium bromide solution was added and the solution was set aside for a certain time before the excess of cerium(IV) was determined iodimetrically. Thus these acids can be oxidised in two stages to carbon dioxide and water. Table II shows the results of oxidation of these acids.

TABLE II

Acid	*Volume of 0.02 M acid (ml)*	*Volume of 0.05 M cerium(IV) solution (ml)*	*Equivalents per mole consumed in photochemical oxidation*[4]	*Volume of 1% potassium bromide solution (ml)*	*Time for complete oxidation (min)*	*Total equivalent of oxygen per mole found*
Malic	1.0	10	8	1.0	100	11.98
Tartaric	1.0	10	6	1.0	100	10.00
Citric	1.0	20	14	1.0	120	18.08

DISCUSSION

It has been observed that formic acid can be oxidised stoichiometrically to carbon dioxide and water by cerium(IV) in presence of a small quantity of potassium bromide. The complete oxidation of those acids which are normally oxidised to the formic acid stage in absence of potassium bromide can also be brought about. In comparison to other procedures used for the oxidation of hydroxy acids by cerium(IV) where the oxidation does not proceed as far as the carbon dioxide stage, the present method has the advantage of yielding more definite products of oxidation. The method is preferable to that involving oxidation of formic acid by standard bromine or bromate–bromide solution because there is no possibility of bromine losses; bromine is generated in very low concentration and is immediately consumed. After the completion of the reaction an amount of bromine equivalent to the potassium bromide added remains in the solution and thus the oxidation may be considered to be brought about indirectly by cerium(IV). This bromine along with the unreacted cerium(IV) liberates an equivalent amount of iodine from potassium iodide. Hence the difference in the amount of iodine liberated by the solution containing formic acid and blank is equivalent to the amount of cerium(IV) used for the oxidation of formic acid. The method can also be used for the complete oxidation of those compounds which give formic acid as the product of oxidation with cerium(IV) under ordinary conditions. The method can also be applied to the complete oxidation of polyhydroxy alcohols and sugars, which will be described shortly.

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SUMMARY

A method is proposed for the determination of formic acid by oxidation with cerium(IV) in presence of potassium bromide. The method can also be used for the further oxidation of organic compounds which yield formic acid under ordinary conditions with cerium(IV).

RÉSUMÉ

Une méthode est proposée pour le dosage de l'acide formique, par oxydation au moyen de cérium (IV), en présence de bromure de potassium. Les auteurs envisagent également le dosage des acides malique, tartrique et citrique.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Ameisensäure durch Oxydation mit Cerium(IV) in Gegenwart von Kaliumbromid. Die Methode kann auch zur Bestimmung von Äpfelsäure, Weinsäure und Citronensäure verwendet werden.

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A NEW RAPID SEMIMICRO TITRIMETRIC DETERMINATION OF MERCURY

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The determination of total mercury, especially in mg amounts, remains a difficult problem. The direct titrimetric method for mercury by means of ammonium thiocyanate[1] is seriously affected by even small amounts of halide ions, which is a considerable drawback. A survey of the literature shows that although considerable work has been done on the determination of mercury in widely different materials, a general simple method applicable to most of its compounds, both inorganic or organic, is not yet available. ROBINSON[2] separated mercury by precipitation with hypophosphorous acid and titrated it with iodine; in this determination, the conditions must be strictly controlled and the results obtained are rather low. Recently BROOKES AND SOLOMON[3] separated mercury from interfering substances by a distillation procedure in which a fused-silica distillation flask is used; the metal was then dissolved in nitric acid and titrated with ammonium thiocyanate solution. The results obtained were comparatively low for small amounts of mercury. The present paper describes a systematic investigation of a simple titrimetric method which is applicable to a wide range of compounds and preparations containing small amounts of mercury, and is relatively free from interferences.

This method, by which small amounts of mercuric ions (0.5 to 5.0 mg) can be determined accurately, is based on titration with potassium iodide solution in presence of sodium bicarbonate; potassium periodate is used as indicator. The reactions are:

$$Hg^{+2} + 2I^- \rightarrow HgI_2 \qquad (1)$$

$$IO_4^- + 2I^- + H_2O \rightarrow IO_3^- + I_2 + 2OH^- \qquad (2)$$

The end-point of reaction (1) is indicated by the colour imparted by iodine (2) to carbon tetrachloride previously added to the mixture. A small amount of potassium or sodium chloride is added to the test solution to prevent the precipitation of mercuric periodate.

EXPERIMENTAL

Mercuric chloride solutions were prepared by weighing accurately small amounts of the chemically pure (A.R.) salt and dissolving them in water.

Procedure for titrating mercury

An aliquot of the mercuric chloride solution containing 0.5 to 5.0 mg of Hg was placed in a glass-stoppered 150 ml conical flask and diluted to about 80 ml with distilled water. Potassium chloride (*ca.* 0.1 g) was added. (This is not necessary if the sample solution is prepared with aqua regia or hydrochloric acid). If necessary, the solution was neutralised cautiously with sodium bicarbonate. Sodium bicarbonate (5 g) was then added followed by 5 ml of a saturated solution of potassium meta-periodate and 3 ml of pure carbon tetrachloride. The volume of the solution was then diluted to approximately 100 ml with water and titrated with 0.01 *N* potassium iodide solution added dropwise at a rate of about one drop per second from a microburette. Towards the end of the titration the solution was shaken for 5–10 sec between each addition. The end-point was indicated by the appearance of the free iodine colour in the organic layer. A blank test was always carried out under the same conditions. One ml of 0.01 *N* potassium iodide is equivalent to 1.003 mg of mercury. The results are shown in Table I.

TABLE I

DETERMINATION OF MERCURY IN DILUTE MERCURIC CHLORIDE SOLUTIONS

No.	*Mercury present (mg)*	*Potassium iodide 0.01 N (ml)*	*Mercury found (mg)*	*Error (mg)*
1	5.0	4.92	4.93	−0.07
2	4.0	4.04	4.05	+0.05
3	3.0	3.04	3.05	+0.05
4	2.5	2.52	2.53	+0.03
5	2.0	2.04	2.05	+0.05
6	1.0	0.95	0.95	−0.05
7	0.64	0.60	0.60	−0.04
8	0.50	0.50	0.50	0.00
9	0.32	0.35	0.35	+0.03

Procedure for decomposing insoluble mercury compounds (inorganic or organic)

Method A. An amount of the substance containing 50–100 mg of mercury was weighed accurately into a dry 500-ml conical flask and 10 ml of aqua regia was added. The flask was covered with a glass and shaken well, and then placed on a hot plate (80°–90°) for about 10–15 min (30–40 min for organic compounds). The flask was then cooled and the solution was diluted to about 200 ml with distilled water. The solution was boiled for 3–4 min, cooled and filtered, if necessary, into a 500-ml measuring flask. The residue, if any, was washed free from chloride and the filtrate was diluted to the mark with distilled water. An aliquot containing 4–5 mg of Hg was taken for the titration.

Method B. In place of aqua regia, the sample could be digested with concentrated nitric acid followed by treatment with chlorine water.

Note. If the content of mercury is less than 50 mg, the digestion is carried out with 5 ml of aqua regia, or with concentrated nitric acid and chlorine water in a 150-ml conical flask, the volume is reduced by evaporation to remove excess acid (if the Hg content is less than 5 mg) and the final volume of the solution is diluted to 100 ml or 50 ml as necessary.

The results obtained for the determination of mercury in various inorganic compounds are shown in Table II.

TABLE II

DETERMINATION OF MERCURY IN VARIOUS INORGANIC COMPOUNDS

Compound	*Mercury present (mg)*	*Mercury found (mg)*	*Error (mg)*
Mercuric oxide	5.0	4.92	—0.08
Mercurous chloride	5.0	4.95	—0.05
Mercuric sulphide	5.0	4.86	—0.14
Mercuric nitrate	5.0	5.06	+0.06
Mercuric sulphate	5.0	5.05	+0.05

Effect of bromide and iodide

For obvious reasons, the present titrimetric method could not be applied in presence of bromide and iodide. For the analysis of mercuric bromide or iodide, bromine and iodine must be removed. Bromine can be removed by boiling the diluted solution after digestion with aqua regia. The removal of iodine is not complete unless the solution is evaporated just to dryness at 80°–90° or in vacuum. The results are shown in Table III.

TABLE III

DETERMINATION OF MERCURY IN MERCURIC BROMIDE OR IODIDE

Compound	*Mercury present (mg)*	*Mercury found (mg)*	*Error (mg)*	*Method of evaporation*
Mercuric bromide	5.0	4.66 (Average of 2 results)	—0.34	
	4.0	3.76 (Average of 2 results)	—0.24	
Mercuric iodide	5.0	4.81 (Average of 2 results)	—0.19	hot evaporation
	4.0	3.66 (Average of 2 results)	—0.34	hot evaporation
	2.0	1.86 (Average of 2 results)	—0.14	hot evaporation
	5.0	4.89	—0.11	vacuum desiccator
	4.0	3.88	—0.12	vacuum desiccator
	2.0	1.96	—0.04	vacuum desiccator

Determination of mercury in presence of impurities

Copper(II), iron(III) and zinc do not interfere, if sufficient periodate is present. The results in presence of iron are somewhat low; better results are obtained if potassium fluoride is added before the addition of bicarbonate. The results are shown in Table IV.

Lead interferes with the titration but good results can be obtained by the following procedure. To the neutral test solution containing mercury (2–5 mg) and lead (0.1 to

TABLE IV

DETERMINATION OF MERCURY IN PRESENCE OF COPPER(II), IRON(III) OR ZINC

No.	*Mercury present (mg)*	*Impurity (g)*	*Saturated KIO_4 solution (ml)*	*Other substances added (g)*	*Mercury found (mg)*	*Error (mg)*
1	5.0	0.05 of $CuSO_4 \cdot 5\ H_2O$	20	—	4.92	−0.08
2	5.0	0.10 of $CuSO_4 \cdot 5\ H_2O$	20	—	4.92	−0.08
3	4.0	0.05 of $CuSO_4 \cdot 5\ H_2O$	20	—	3.91	−0.09
4	4.0	0.10 of $CuSO_4 \cdot 5\ H_2O$	20	—	3.91	−0.09
5	4.0	0.05 of Fe(III)	25	—	3.61	−0.39
6	4.0	0.05 of Fe(III)	25	2.5 of KF	3.91	−0.09
7	5.0	0.05 of Fe(III)	25	2.5 of KF	4.91	−0.09
8	5.0	0.1 of Fe(III)	25	5.0 of KF	5.02	+0.02
9	4.0	0.05 of $ZnSO_4 \cdot 7\ H_2O$	20	—	3.91	−0.09
10	4.0	0.1 of $ZnSO_4 \cdot 7\ H_2O$	20	—	3.96	−0.04

0.3 g), potassium chloride (0.3 to 0.5 g) was added followed by potassium dihydrogen phosphate (0.3 to 0.5 g). The solution was then titrated as usual after addition of bicarbonate. The results are recorded in Table V.

TABLE V

DETERMINATION OF MERCURY IN PRESENCE OF LEAD

Lead compound $Pb(NO_3)_2$ (g)	*Potassium chloride (g)*	*KH_2PO_4 (g)*	*Mercury present (mg)*	*Mercury found (mg)*	*Error (mg)*
0.15	0.3	0.3	2.0	1.90	−0.10
0.25	0.3	0.3	2.0	1.95	−0.05
0.15	0.3	0.3	4.0	3.90	−0.10
0.25	0.3	0.3	4.0	3.90	−0.10
0.50	0.5	0.5	5.0	5.05	+0.05
0.50	0.5	0.5	5.0	5.15	+0.15

Moderate amounts of cations and anions such as Ca^{+2}, Mg^{+2}, Al^{+3}, SO_4^{-2}, AsO_4^{-3}, $H_2PO_4^-$ and NO_3^- do not interfere.

Organic mercury compounds have also been accurately analysed by this method. The results are compared with the calculated values of mercury obtained by other methods and are shown in Table VI.

TABLE VI

DETERMINATION OF MERCURY IN ORGANIC COMPOUNDS

Compound	*Mercury found (mg)*		*Mercury calc. (mg)*	*Mean error (mg)*	*Reagents used for decomposition*
Ethylmercuric chloride	3.56	3.56	3.70	0.14	aqua regia
	3.61	3.51	3.70	0.14	conc. HNO_3, Cl_2 water
Phenyl mercuric chloride	3.01	3.01	3.15	0.14	aqua regia
	3.01	3.06	3.15	0.11	conc. HNO_3, Cl_2 water
Mercurochrome	4.14	4.14	4.21	0.07	aqua regia[a]

[a] The residue obtained by evaporation of 2 ml of a 1% solution of mercurochrome to dryness can be decomposed easily by digestion with 2 ml of aqua regia.

Proprietary brands of mercury-containing pesticides

Owing to the difficulty of preparing small samples of pesticides accurately in the laboratory, two proprietary brands were analysed by this titrimetric method. The results are shown in Table VII.

TABLE VII

DETERMINATION OF MERCURY IN PESTICIDES

Material	*Mercury found (%)*	*Mercury found by other methods (%)*	*Reagents used for decomposition*
Ceresan (Bayer)	2.81 (Average of 2 results)	2.84	aqua regia
	2.87 (Average of 3 results)	—	conc. HNO_3
	3.01 (Average of 2 results)	—	conc. HNO_3, Cl_2 water
Agrosan GN (I.C.I.)	0.91 (Average of 2 results)	0.90	aqua regia[a]

[a] Satisfactory results were not obtained when this compound was decomposed with nitric acid.

CONCLUSIONS

The proposed titrimetric procedure for the determination of small amounts of mercury can be applied to a wide range of preparations. The method is especially advantageous for the assay of 0.01 to 0.001% mercuric chloride solutions. The procedure is simple and rapid, and the majority of preparations can be analysed in 15 to 30 min. With preparations containing organic substances, 40–45 min are required for analysis.

The results obtained in all the analyses, except those for mercuric bromide or iodide, are well within the limits of error permissible in semimicro or micro analysis.

SUMMARY

Mercury(II) (0.5 to 5 mg) can be determined accurately by titration with potassium iodide solution in presence of potassium periodate and carbon tetrachloride as indicator. The simple and rapid method is applicable to many mercurial compounds and preparations; interferences are few.

RÉSUMÉ

Une semi-micro méthode est proposée pour le dosage volumétrique du mercure(II), au moyen d'iodure de potassium. Ce procédé est simple et rapide.

ZUSAMMENFASSUNG

Beschreibung einer einfachen und raschen Halbmikro-Methode zur volumetrischen Bestimmung von Quecksilber(II) mit Kaliumjodid.

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HYDRAZINE AS A TITRIMETRIC REAGENT IN IODOMETRY

PART I

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Direct and indirect iodometric procedures are very widely used both in inorganic and organic analysis[1] but the traditional methods possess certain disadvantages. Standard iodine solution can be prepared by direct weighing[2] but this is somewhat inconvenient and therefore standardisation of an approximate solution is usually preferred. Arsenic trioxide is a well-established iodimetric primary standard but its use is generally limited to the standardisation of iodine solution and the preparation of standard arsenite solution is laborious. Sodium thiosulphate solution[3] is commonly used for the determination of free iodine; however, unless care is taken during its preparation, standardisation and storage, the reagent is not satisfactory. Moreover, there is a possibility of side-reactions owing to atmospheric oxidation and acid decomposition of the titrant. A general study of the disadvantages of thiosulphate, and to some extent sodium arsenite, has been made by BANKS[4].

A survey of methods showed that previous work has aimed either at determining hydrazine[5] itself or at its use as a direct reductant[6]. Because of the limitations of arsenite and thiosulphate solutions an attempt has been made to study the general behaviour of hydrazine as a reagent in iodometric titrations. This is not a new application[7] and no originality is claimed in this respect; however, we have studied the general use of the reagent in iodometry, as well as the optimum conditions for the iodometric determination of various substances. The direct and indirect determinations of a large number of substances are described below.

EXPERIMENTAL

Preparation, standardisation and stability of hydrazine solution

Free hydrazine base itself is unstable[8] but its hydrochloride and sulphate salts are quite stable. Analytically pure[5] salts can be easily prepared by recrystallisation of the C.P. product from water.

A 0.1 *N* solution of hydrazine was prepared by dissolving 2.6237 g of pure hydrazine hydrochloride (B.D.H.) in 1 l of glass-distilled water. The solution was stored in glass-stoppered bottles. Its concentration was checked by titrating against an iodine solution which had been standardised against sodium arsenite and bromate solution. The solution was highly acidic (pH 1.4 to 2) and was quite stable. The change in titre of the solution corresponded to only 0.05 ml of 0.1 *N* iodine solution when 100 ml were titrated after standing for a week.

General method for titrating excess or liberated iodine with hydrazine solution

The reaction between hydrazine and iodine is slow in acid medium[9] but rapid in presence of bicarbonate[10] (pH 7 to 7.4); excess of bicarbonate should be avoided because high results are obtained at high pH values owing to decomposition of hydrazine. A suitable amount of bicarbonate is 0.5–1 g per 25 ml of 0.1 *N* hydrazine solution. After iodine has been liberated from an aliquot of the test solution by adding potassium iodide in acid or neutral medium, the solution is neutralised with sodium bicarbonate. The titration is then carried out in presence of a slight excess of bicarbonate, the end-point being detected by the usual starch or starch glycollate indicator. Near the end-point the reaction is rather slow and the titrant must be added slowly with stirring. If the colour of the starch–iodide complex is obscured by the presence of other coloured substances, the end-point can be detected by the potentiometric "dead-stop" technique[11]. Sargent's Electrometric Titration Apparatus 'Ampot' with two similar platinum electrodes at an applied polarising potential of 20–30 mV was used in the present work. In presence of iodine the electrodes remain depolarised as indicated by a current of 15–20 mA flowing through the cell. In presence of excess of hydrazine the electrodes are polarised and the current reduces nearly to zero. Both the visual indicator method and the "dead-stop" technique gave identical and reproducible results but the latter method is to be preferred because of certain disadvantages of the starch indicator.

Permanganate, dichromate and cerium(IV)

In acidic medium dichromate, permanganate and cerium(IV) are reduced to definite lower valency states (Cr = 3, Mn = 2 and Ce = 3) by hydriodic acid, liberating equivalent amounts of iodine. After the free acid has been neutralised with bicarbonate, the liberated iodine can be titrated with standard hydrazine solution as described above. Sufficient sample should be taken to consume 5–25 ml of 0.1 *N* hydrazine, when the results are precise to ± 0.3 to $\pm 0.6\%$.

Copper sulphate

Iodine is liberated from solutions containing no free mineral acid by adding 1 g of potassium iodide per 0.6 g of copper sulphate present. The reaction mixture is then neutralised and titrated as above. The results are precise to $\pm 0.5\%$.

Chlorate

To 10 ml of chlorate solution (*ca.* 0.2 *N*) are added 1 g of potassium bromide and 20 ml of concentrated hydrochloric acid (the final acid concentration should be 8 *N*). The flask is stoppered and allowed to stand for 5 min; 10 ml of 10% potassium iodide solution are then added and the titration is completed as before.

Bromate and iodate

Iodine is liberated from an aliquot of the test solution containing 0.5–2.5 mequiv. of bromate or iodate by adding 1 g of potassium iodide and sufficient hydrochloric acid, and the iodine is titrated as described earlier. In the case of bromate the reaction is slow and the reaction mixture should be allowed to stand for 2 min before the liberated iodine is titrated. The results are precise to ± 0.3 to $\pm 0.5\%$.

Periodate

To a solution of periodate containing 0.5 mmoles of the salt, 20 ml of saturated borax solution containing 0.5 g of boric acid are added followed by 2 g of potassium iodide; the liberated iodine is titrated as described above.

Hypochlorite and bleaching powder

2 g of potassium iodide and 10 ml of glacial acetic acid are added to the test solution and the liberated iodine is titrated as before.

Selenite

To 20 ml of approximately 0.05 *N* selenite solution are added 150 ml of water, 15 ml of starch solution, 10 ml of *N* potassium iodide and 10 ml of 5 *N* hydrochloric acid. The reaction mixture is allowed to stand for 15 min to complete the reduction of selenite to selenium and then titrated after neutralisation.

Hydrogen peroxide

To a 25-ml portion of *ca.* 0.1 *N* peroxide are added 10 ml of 4 *N* sulphuric acid and 6 ml of *N* potassium iodide followed by 3 drops of ammonium molybdate solution, and the liberated iodine is titrated as before. If ammonium molybdate is not added as catalyst, the reaction mixture should be allowed to stand for 15 min in a closed vessel before titration. The method can also be applied to metallic peroxides.

Ferricyanide and zinc

To 25 ml of a solution containing *ca.* 0.1 g of ferricyanide are added 20 ml of 10% potassium iodide, 2 ml of 2 *N* hydrochloric or sulphuric acid and 15 ml of a solution containing 2 g zinc sulphate. Liberated iodine is then titrated after neutralisation. Zinc sulphate[12] is added to prevent the back-reaction involving the conversion of ferrocyanide to ferricyanide.

By suitable modification, *i.e.* by employing an excess of ferricyanide and a definite amount of zinc solution, the method can also be employed for the determination of zinc.

Manganese dioxide

To a suspension of 150 mg of the powdered dioxide and 20 ml of 4 *N* phosphoric acid in a glass-stoppered flask is added sufficient bicarbonate to remove air followed by 1.5 g of potassium iodide. The flask is allowed to stand till all the dioxide has dissolved. The liberated iodine is then titrated as usual after neutralisation with sodium bicarbonate.

Sulphide, sulphite, phosphite and nitrite

Sulphide, sulphite, phosphite and nitrite are oxidised in acidic medium by standard iodine solution to sulphur, sulphate, phosphate and nitrate respectively but iodate–iodide mixture is preferable as a source of iodine. The solution containing 2.5 mmoles of the salt is mixed with the iodate–iodide mixture and then acidified. The excess iodine is then titrated as usual after standing for some time.

Mercurous mercury

To about 240 mg of mercurous chloride 25 ml of 0.1 *N* iodine and 1 g of potassium iodide are added and the mixture is shaken till the precipitate dissolves completely. It is then titrated as usual after neutralisation.

Ferrous iron

To the ferrous solution are added 5 ml of 4 *N* sulphuric acid and sufficient sodium bicarbonate to remove air from the flask; 5 g of powdered sodium pyrophosphate[13] are then added and the mixture is stirred till all the salt has dissolved. Iodine is then added and back-titrated after standing for a few seconds in the usual way.

Ferrocyanide

To about 25 ml of a solution containing 5–25 mmoles of ferrocyanide in an Erlenmeyer flask, are added 25 ml of 10% disodium monohydrogen phosphate solution, 25 ml of 20% acetic acid and 25 ml of 0.1 *N* iodine solution. The reaction mixture is then left in the dark for about 15–20 min and excess of iodine is titrated as usual.

Mercuric mercury

To 200 mg of mercuric chloride, 1–2 g of potassium iodide are added and shaken till the precipitate dissolves; 10 ml of 4 *N* sodium hydroxide solution and 3 ml of 35% formaldehyde are then added with continuous shaking, followed by 10 ml of water. After 2 min 10 ml of acetic acid and 25 ml of 0.1 *N* iodine solution are added. The reaction mixture is shaken till all the mercury dissolves and then excess of iodine is titrated after neutralisation.

DISCUSSION

The quantitative reaction of hydrazine and iodine is well established and in presence of a slight excess of sodium bicarbonate (pH = 7.4) the reaction proceeds rapidly and smoothly. The present study has shown that hydrazine can also be used for the titration of iodine liberated from iodide by certain oxidants such as permanganate, dichromate and cerium(IV), as well as for the determination of excess of iodine left after the oxidation of certain reductants.

It has been established that the reduction products of certain oxidants, *i.e.* Mn^{+2}, Cr^{+3}, Ce^{+3}, Zn^{+2}, Se, Cu_2I_2, Cl^-, Br^-, I^-, and oxidation products of certain reductants, *i.e.* Fe^{+3}, S, SO_4^{-2}, NO_3^-, PO_4^{-3} etc. do not interfere in the hydrazine–iodine reaction. Hydrazine can therefore be recommended as a suitable reagent in the iodometric determination of these compounds. Interference was observed in two cases, *i.e.* when ferric or ferrocyanide ions are present but this can be eliminated by complexing with phosphate or zinc ions respectively. Additional advantages of hydrazine salts are their availability in an analytically pure form which can be used as a primary standard, the stability of their solutions and the uniform conditions of the reaction with iodine. The disadvantage is that the cost of the reagent is higher than that of sodium thiosulphate. Iodometric determinations of other compounds, including organic substances, is under investigation and the results will be communicated shortly.

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The authors express their sincere thanks to Prof. K. P. HALDAR for his keen interest in the work.

SUMMARY

The preparation, standardisation and stability of hydrazine solution is described. The optimum conditions for the titration with hydrazine solution of pure iodine solution of iodine liberated from oxidants and of excess of iodine left after oxidation of certain reductants have been determined. The advantages of hydrazine over other iodometric reagents are discussed.

RÉSUMÉ

L'hydrazine peut être utilisée comme réactif pour le titrage iodométrique de nombreuses substances. Dans cette première partie, les auteurs ont examiné la préparation, l'étalonnage et la stabilité des solutions d'hydrazine.

ZUSAMMENFASSUNG

Beschreibung der Herstellung, Standardisierung und Stabilität von Hydrazinlösungen, deren Titration mit Jodlösung und Anwendung bei der Bestimmung von Oxydations- und Reduktionsmittel.

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REDOX INDICATORS IN INDIRECT TITRATIONS OF ANIONS. DETERMINATION OF PHOSPHATE IONS BY MEANS OF LEAD NITRATE

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INTRODUCTION

Titration of phosphates is normally accomplished by complexometric or alkalimetric methods. However, recently, it was proposed that anions could be titrated indirectly by means of lead(II) nitrate in presence of redox indicators[1] the excess of lead being titrated with potassium ferrocyanide. Determinations of sulphate[2] and chromate[3] ions are also possible on this basis.

In the present paper, a similar indirect determination of phosphate ions is described. Excess of lead ions are titrated with potassium ferrocyanide solution in presence of variamine blue as a redox indicator. Previously, the same redox indicator[4] was used in the direct determination of phosphate ions with ferric nitrate, but this procedure does not give very accurate results and has many drawbacks.

EXPERIMENTAL

Reagent

1% Variamine blue solution (4-amino-4'-methoxydiphenylamine-acetate) in 20% acetic acid

Procedure

Two alternative methods are available:

(*a*) To the test solution of phosphate 2 ml of 1 *N* ammonium acetate, 2 ml of 1 *N* acetic acid and several ml of methyl alcohol were added. After this solution had been heated to boiling, excess of 0.1 *N* lead(II) nitrate was added dropwise with mechanical stirring. For high concentrations of phosphate ions 1 *N* lead nitrate solution was used. The solution was again boiled (to coagulate the precipitate) and then cooled, and the precipitate was filtered on a G4 crucible. It was then washed with an aqueous solution of methyl alcohol in such amounts that the final volume before titration was 100 ml and the methyl alcohol content amounted to 25%.

The filtrate was heated to about 60° and 3 drops of variamine blue solution and one drop of 0.1 *N* potassium ferricyanide were added. The sample was titrated with 0.1 *N* potassium ferrocyanide until the violet-blue colour changed to a permanent pale yellow; mechanical stirring was used.

(*b*) In the second method, the precipitate was not filtered. Otherwise the phos-

phate was determined as given in method (*a*), the same volume of solution (100 ml) and the same methyl alcohol content being used.

The same results were obtained in both cases.

Effect of foreign ions

Di- and trivalent cations interfere because they form insoluble phosphates and cannot be removed with alkali metal carbonates. Univalent cations interfere when their amount is greater than 5 times that of the excess of lead nitrate[2]. Anions which form precipitates with lead nitrate in presence of acetic acid also interfere.

DISCUSSION OF RESULTS

The influences of dilution and of the methyl alcohol content were tested. Under optimal conditions the reproducibility of results for the range 10–150 mg of phosphate is approximately 1.5%. The ferrocyanide solution must be standardized under identical conditions.

The results obtained by this titrimetric method agree with those of gravimetric determinations of phosphate as magnesium pyrophosphate (Table I).

TABLE I

GRAVIMETRIC AND TITRIMETRIC DETERMINATION OF PHOSPHATE IONS

Sample	*Determination*		*Error*	
	Gravimetric mg	*Titrimetric*[a] mg	mg	%
1	178.5	175.0	—3.5	—1.96
2	176.3	174.0	—2.3	—1.30
3	176.1	174.0	—2.1	—1.19
4	176.0	174.0	—2.4	—1.10
5	175.1	174.0	—1.1	—0.63

[a] The volume of solution taken was only a fifth of that used for the gravimetric method.

SUMMARY

An indirect titration of phosphate with lead(II) nitrate solution is proposed; excess of lead is titrated with potassium ferrocyanide in presence of variamine blue as redox indicator.

RÉSUMÉ

Une méthode a été mise au point pour le dosage volumétrique indirect des phosphates par le plomb, dont on titre l'excès au moyen de ferrocyanure de potassium.

ZUSAMMENFASSUNG

Beschreibung einer volumetrischen Methode zur Bestimmung von Phosphat mit einer Bleisalzlösung, deren Überschuss mit Kaliumferrocyanidlösung zurücktitriert wird.

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CHELATES OF 4-HYDROXYBENZOTHIAZOLE WITH THE RARE EARTHS

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The reactions of several types of chelating agents with the rare earths have been investigated in recent years. Among the more important ligands that form chelates with the rare earths are dicarboxylic acids[1], amino acids[2], aminopolycarboxylic acids[3,4], β-diketones[5], cupferron[6], neocupferron[6], and 8-hydroxyquinoline and some of its derivatives[7]. Some workers have claimed that most of the rare earths form 1 : 3 chelates with 8-hydroxyquinoline[7,8]. However it has subsequently been shown that it is quite difficult to prepare rare earth oxinates having the expected 1 : 3 stoichiometry[9]. This is probably due to the contamination of these metal chelates with basic hydrolytic products of the rare earth cations.

Although 8-hydroxyquinoline and 4-hydroxybenzothiazole have similar chelate forming functionalities, the latter is more selective since it will not react with titanium, vanadium, molybdenum and tungsten[10]. The investigation of the chelating tendencies of 4-hydroxybenzothiazole towards the rare earths is an extension of the previous work carried out in this laboratory in order to evaluate the factors that give rise to the selectivity of 4-hydroxybenzothiazole[11].

EXPERIMENTAL

Preparation of metal solutions

Stock solutions of the lanthanides were prepared by dissolving weighed amounts of metals or their oxides in nitric acid and diluting to an appropriate volume with water. Table I gives the purity of the materials used. The solutions were not standardized.

TABLE I

PURITY OF METALS AND METAL OXIDES USED

Metal or metal oxide	*% Purity*
Y_2O_3, Pr_6O_{11}, Nd_2O_3, Tb_4O_7, Er_2O_3, Tm_2O_3, Yb_2O_3, Lu_2O_3	99.9
La, Gd	99.6
Ce	98
Sm	99.97
Eu_2O_3	99.8
Dy	99.5
Ho	99.3

Hydrolysis of metal nitrates in 50% v/v ethanol–water

A measured volume of the metal nitrate solution was made up to contain 50% v/v of ethanol and titrated with 0.1 *M* carbonate-free sodium hydroxide at 25 ± 0.2°. The solution was first degassed with nitrogen and an atmosphere of nitrogen was maintained in the titration vessel throughout the titration. After the excess acid in the metal nitrate solution was neutralized, the standard sodium hydroxide was added in small increments (0.1–0.2 ml). A volume of ethanol equal to the volume of the standard base was added after each increment, in order to maintain the ethanol–water ratio at 50% v/v. The pH of the solution was measured not less than 10 min after each addition of standard base in order to ensure that equilibrium was reached. All pH measurements were made with a Beckman Model G pH meter equipped with a glass–saturated calomel electrode pair and calibrated with buffer solutions at pH 4.00 and 7.00. From the titration curves obtained, the pH values at which the metal ions hydrolyzed could be determined.

Preparation of metal chelates

The preparation of 4-hydroxybenzothiazole has been published[11]. A 0.1-*M* solution of 4-hydroxybenzothiazole in ethanol was added to the metal nitrate solution. The resulting solution contained about 50% v/v of ethanol and a 4 : 1 ratio of 4-hydroxybenzothiazole: metal ion. The pH of the solution was raised slowly and with stirring by the dropwise addition of 1 : 1 ammonia. The pH at which the first permanent precipitate was obtained was noted and 2 to 3 drops more of ammonia solution was added. In all cases the pH at which the metal chelate precipitated was below the pH at which hydrolysis of the metal ion occurred. The resulting solution was warmed on a water-bath until the precipitate coagulated. The solution was filtered and the precipitate washed with water and ethanol. The chelates were dried in a vacuum desiccator to constant weight and analyzed.

Titrimetric determination of 4-hydroxybenzothiazole

A weighed amount of 4-hydroxybenzothiazole was dissolved in 2 *N* hydrochloric acid and a measured excess of standard potassium bromate–bromide solution added, the excess being determined iodometrically with starch as the indicator. The precision and accuracy obtained in this bromometric titration of 4-hydroxybenzothiazole was unsatisfactory, especially for the titration of small quantities of 4-hydroxybenzothiazole. All determinations were subsequently carried out using an amperometric indicator circuit for the detection of the end-point[12].

A stock solution containing 0.15 mg of 4-hydroxybenzothiazole per ml was made in 1 *N* hydrochloric acid. An aliquot of this solution was added to the titration vessel together with 1 g potassium bromide. The total volume was made up to about 40 ml, sufficient hydrochloric acid being present in the solution to make the solution about 1 *N* in hydrochloric acid. The titrant was 0.002 *M* potassium bromate in 0.1 *M* potassium bromide. A rotating platinum microelectrode, rotated with a Sargent synchronous motor, was used as the indicator electrode. This indicator electrode and a standard calomel electrode were placed in the titration vessel, and short-circuited through a microammeter. The potential of the saturated calomel electrode was sufficiently negative for the current in the indicator system to be proportional to the amount

of free bromine in solution. A plot of current *vs.* volume of titrant gave an L-shaped titration curve from which the end-point was readily located. No correction for a blank titration was applied, since this was negligibly small. In all titrations a correction was made for the volume change that occurred during the titration.

Titrimetric determination of 4-hydroxybenzothiazole chelates

A weighed amount of the chelate was dissolved in 12 *N* hydrochloric acid and diluted to an appropriate volume in a volumetric flask with distilled water. Aliquots of this solution were used for the bromometric titration as described for 4-hydroxybenzothiazole. All solutions titrated were about 1 *N* in hydrochloric acid. The results obtained are given in Table II, each result being the average of 2–4 determinations.

TABLE II

TITRIMETRIC DETERMINATION OF THE RARE EARTH CHELATES OF 4-HYDROXYBENZOTHIAZOLE

Metal	*% Ligand found*	*% Ligand calculated for 1 : 3 chelate*
La	76.10	76.42
Pr	73.63	76.17
Nd	75.20	75.74
Sm	72.53	74.97
Eu	74.10	74.76
Gd	71.26	74.12
Tb	73.82	73.91
Dy	67.61	73.48

Gravimetric determination of 4-hydroxybenzothiazole chelates

The rare earth chelates of 4-hydroxybenzothiazole were ignited in a Pregl micro-muffle furnace and weighed as the oxides. The results of several determinations are averaged and given in Table III.

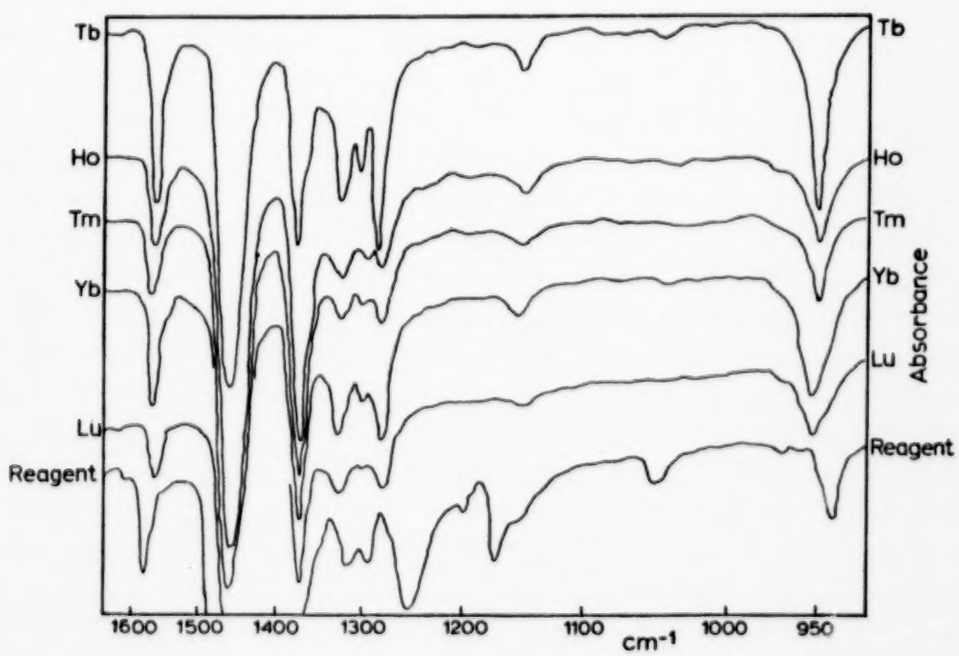

Fig. 1a.

Infrared spectra of 4-hydroxybenzothiazole chelates

All spectra were recorded with a Perkin Elmer Model 21 double-beam spectrophotometer equipped with sodium chloride optics, employing Nujol mulls of the metal chelates. The infrared spectra obtained are shown in Fig. 1 and summarized in Table IV.

RESULTS

Since the solubility of 4-hydroxybenzothiazole in water was low, a solution of the compound in ethanol was used for precipitating the chelates from aqueous solutions

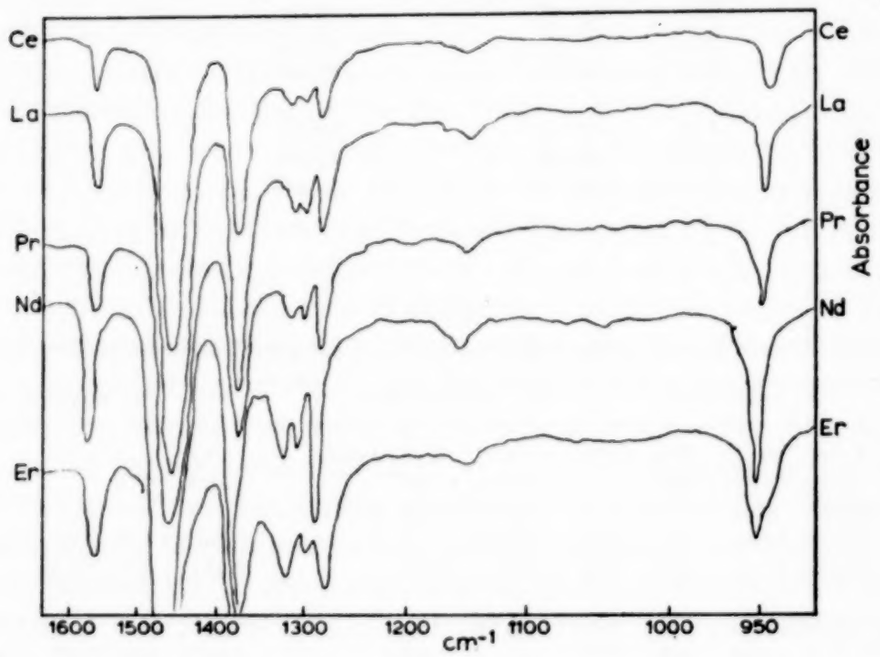

Fig. 1b.

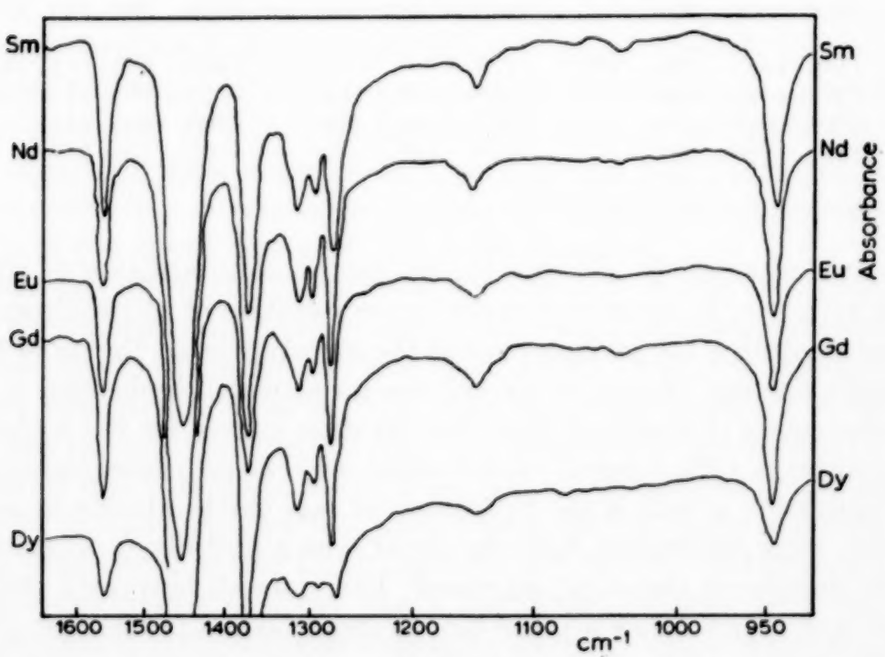

Fig. 1c

Fig. 1. Infrared spectra of the rare earth chelates of 4-hydroxybenzothiazole.

TABLE III

MICROGRAVIMETRIC DETERMINATION OF THE RARE EARTH CHELATES OF 4-HYDROXYBENZOTHIAZOLE

Metal	*% Metal found*	*% Metal calculated for 1:3 chelate*
Ce	24.46	23.73
Pr	20.99	23.83
Nd	24.43	24.26
Sm	23.73	25.03
Eu	24.95	25.24
Gd	24.82	25.88
Tb	21.46	26.09
Dy	24.16	26.52
Ho	26.76	26.81
Er	26.92	27.08
Tm	27.37	27.28
Yb	29.94	27.76
Lu	27.79	27.98

TABLE IV

INFRARED SPECTRA OF RARE EARTH CHELATES OF 4-HYDROXYBENZOTHIAZOLE

Metal chelate	*Strong cm⁻¹*	*Medium cm⁻¹*	*Weak cm⁻¹*
La	1553, 944, 765, 1276	1310, 1148, 1294	717
Ce	1555, 1278, 946	1312, 1148	1296, 718
Pr	1558, 946, 1278	1310, 766, 1296	718
Nd	1560, 1280, 947, 767	1312	1298, 1150, 827, 805, 719
Sm	1560, 1278, 945, 764	1313, 1147	1294, 826, 805
Eu	1560, 1280, 947, 766	1317, 1150	1298, 807, 746, 717
Gd	1563, 1280, 948, 766	1317, 1150	1297, 806, 738, 719
Tb	1560, 947, 1277, 765	1318, 1150	1298, 881, 827, 809, 738, 717
Dy	1562, 1277, 947	1316, 765	1294, 736, 717
Ho	1560, 1278, 947	1318, 1146, 763	1293, 883, 733, 718
Er	1563, 1277, 950, 765	1320, 1150	1295, 883, 805, 732
Tm	1563, 1278, 948	1320, 1148, 764	1293, 885, 734, 718
Yb	1565, 950, 1276	1323, 1150, 765	1295, 805, 732
Lu	1565, 1278, 952	1320, 1148, 763	1295, 733, 718

of the rare earth nitrates. In all cases the maximum concentration of ethanol in the solution was 50% v/v. In order to prevent coprecipitation of any hydrolysis products of the rare earths during the precipitation of the metal chelates, the pH of the ethanol–water solutions was not allowed to exceed the pH at which hydrolysis occurred. The latter pH values were determined from the titration curves for the hydrolysis of the rare earth nitrates in 50% ethanol–water solutions. The pH values reported by MOELLER AND KREMERS[13], at which the hydrolysis of rare earth nitrates in aqueous solutions occurred, were confirmed. Also the pH at which hydrolysis occurred decreased as the atomic number of the metal increased. Therefore all rare earth chelate precipitations were carried out below a pH of 6.0. In most cases a permanent precipitate of the rare earth chelate with 4-hydroxybenzothiazole was formed at a pH between 4.5 and 5.5.

It was found necessary to devise a method for the determination of 4-hydroxybenzothiazole in its chelates. A bromometric titration based on the formation of the 5,7-dibromo compound[14] was found to be unreliable if starch solution was used as the indicator. However using an amperometric indicator system it was found that a $1.5 \cdot 10^{-4}$ *M* solution of 4-hydroxybenzothiazole could be titrated with an error of less than 1%. This method was employed for the determination of 4-hydroxybenzothiazole in some of its rare earth chelates. The results are summarized in Table II.

DISCUSSION

From the analytical results shown in Table II it is probable that most of the rare earth chelates of 4-hydroxybenzothiazole have a 1 : 3 metal : ligand ratio although there are several cases in which the data are difficult to interpret. Both titrimetric and gravimetric methods give low results for the chelates of Pr, Dy, Gd and Sm. It is possible that in these cases a definite number of moles of water are associated with the chelates. Any attempts to remove this water by drying at elevated temperatures resulted in the decomposition of the chelates. If it is assumed that three moles of water are associated with the Dy chelate and two moles of water with the Gd and Sm chelates, the calculated values in Tables II and III agree reasonably well with experimental values. On the other hand it is quite possible that in the case of Pr, a non-stoichiometric complex was formed since Pr_6O_{11} was the source of the praseodymium ion which may have existed in solution in more than one oxidation state. The low result obtained gravimetrically for the percentage of Tb in its chelate was probably due to a mixture of oxides formed when the chelate was ignited in the micromuffle furnace. The titrimetric method using an amperometric indicator circuit gave poor results for the chelates of Ce, Ho, Er, Tm and Yb. It was found that errors of about 10% were obtained and in addition there was considerable difficulty in locating the end-point in the titration in the presence of these rare earths.

It has become apparent from this work that 4-hydroxybenzothiazole is not a particularly suitable reagent for either the separation or determination of the rare earths. Most of the rare earth chelates are precipitated in approximately the same pH range and it is evident that it is quite difficult to prepare stoichiometric complexes and also to avoid coprecipitation of hydrolysis products of the rare earths. In spite of the fact that the pH at which these chelates were precipitated was below the pH at which hydrolysis occurred, it is nevertheless possible that some contamination with hydrolytic products of the metal ions may have been obtained.

The infrared spectra of the chelates of the elements in the first transition series with 4-hydroxybenzothiazole were examined and empirical assignments made for the C–O vibrations in the chelates[11]. It was therefore of interest to determine whether these assigned frequencies could be located in the infrared spectra of the rare earth chelates. On the basis of the shifts of the C–O vibration frequencies in the transition metal chelates, it was found possible to make certain qualitative predictions concerning the stability of these chelates[11]. A similar attempt was made to correlate the chelate stability with shifts in the C–O vibration frequencies in the rare earth metal chelates of 4-hydroxybenzothiazole. Fig. 1 and Table IV give the results obtained.

The infrared spectra of the rare earth chelates are very similar to one another, as is to be expected, if all the compounds contain a 1 : 3 metal : ligand ratio. The strong band between 1555 cm^{-1} and 1565 cm^{-1} as well as the band of medium intensity between

1310 cm^{-1} and 1320 cm^{-1} can be attributed to C–O vibrations in these chelates[11]. The positions of these bands are shifted by only 10 to 15 cm^{-1} in going from the lanthanum to the lutecium chelate. This is an extremely small shift corresponding to an energy difference of 30–45 cal and any correlations that can be made would be fortuitous. However it can be seen that there is a general tendency for this band to shift to higher wave numbers with increasing atomic weight or atomic number. This is suggestive of the fact that there may be little change in the stability constants of the chelates of the metals in this series, and the changes if any would tend to make the rare earths of higher atomic number form more stable chelates than those of lower atomic number.

ACKNOWLEDGEMENT

The authors are grateful to the U.S. Atomic Energy Commission for financial assistance.

SUMMARY

The rare earth chelates of 4-hydroxybenzothiazole have been prepared and analyzed by a titrimetric method as well as a microgravimetric method. The infrared spectra of these chelates have been determined.

RÉSUMÉ

Les auteurs ont effectué une étude sur les chélates de l'hydroxy-4-benzothiazole obtenus avec les terres rares.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Chelate der seltenen Erden mit 4-Hydroxybenzothiazol.

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MICRODOSAGE COLORIMÉTRIQUE DU BORE EN MILIEU AQUEUX, AU MOYEN DE RÉACTIFS À GROUPEMENT AZOÏQUE OU IMINE DÉRIVÉS DES ACIDES H ET K

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(Reçu le 4 octobre 1960)

Les réactions servant au dosage colorimétrique de petites quantités d'acide borique, très sensibles et spécifiques, ont généralement toutes le défaut de ne pouvoir être développées en milieu aqueux, et la pollution par l'humidité des milieux réactionnels peut, en certains cas, fausser gravement les dosages.

On s'est proposé d'étudier les réactions colorées permettant le micro-dosage colorimétrique du bore en milieu aqueux; elles sont peu nombreuses et ne semblent guère avoir été utilisées jusqu'ici: à citer celle à l'acide chromotropique mentionnée par KUEMMEL ET MELLON[1], encore que la sensibilité de cette réaction semble être assez moyenne.

Le présent travail a pour origine les réactions colorées indiquées par KORENMAN[2], KORENMAN ET SHOGANOVA[3], POLUEKTOV ET NIKONOVA[4]. Ces auteurs envisagent, il est vrai, quelques réactions colorées, au reste classiques, que donne l'acide borique, en milieu aqueux et alcalin, avec l'aluminon ou avec des dérivés hydroxy-anthraquinoniques (alizarine, quinalizarine, etc.); la sensibilité de tels réactifs est faible, la dilution limite est seulement 1 pour 10,000, et atteint rarement 1 pour 100,000. Il n'en sera pas traité dans ce qui suit: les réactifs opérant en milieu aqueux et acide présentent, en effet, un intérêt beaucoup plus net.

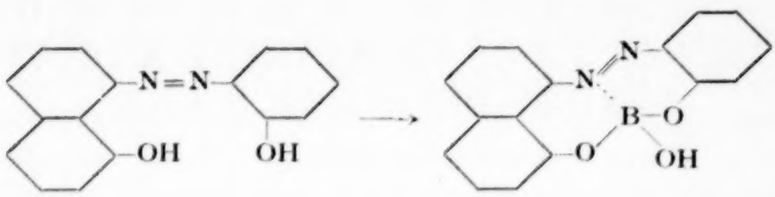
Sont rappelées ci-après les règles établies expérimentalement par POLUEKTOV ET NIKONOVA[4], s'agissant de la structure des réactifs qui donnent des colorations en milieu aqueux acide. Ceux-ci résultent de la combinaison des acides amino-α naphtol-disulfoniques avec un phénol par l'intermédiaire d'une fonction azoïque ou d'une fonction imine.

Ne réagissent pas avec l'acide borique, les oxyazoïques contenant un seul hydroxyle ou encore plusieurs hydroxyles sur le même noyau, par exemple: le dérivé obtenu à partir de la *m*-nitroaniline diazotée avec le phénol.

Ne réagissent pas non plus avec l'acide borique, les azoïques où deux hydroxyles sont dans deux noyaux différents, en *ortho* par rapport au groupement azoïque, par exemple: le dérivé obtenu à partir de l'acide amino-1-naphtol-2-sulfonique-4 et de la résorcine.

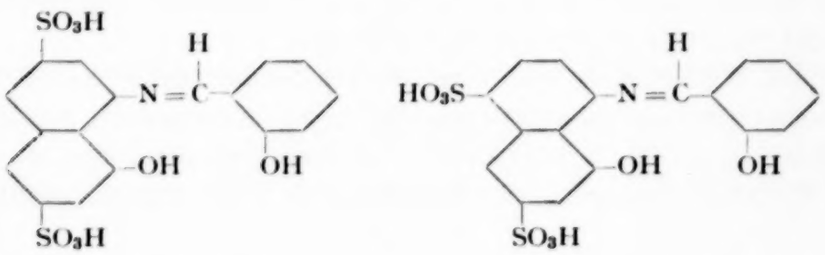
Par contre, donnent une réaction colorée avec l'acide borique les azoïques comportant dans un noyau naphtalénique un OH en péri par rapport au groupement azoïque, et sur l'autre noyau (naphtalénique ou phénylé) un OH en *ortho*. La réaction consiste

en un virage, qui a lieu par chauffage en milieu acétique à 80–100°, puis refroidissement. Il s'agit vraisemblablement d'une chèlation par le bore, portant les oxydriles, par exemple:

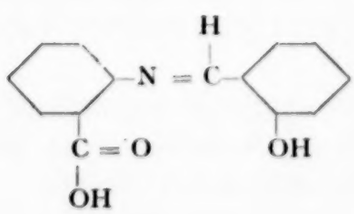


Dans les réactions colorées obtenues avec les réactifs du type azoïque l'on peut, selon KORENMAN[2,3], POLUEKTOV ET NIKONOVA[4], remplacer le groupement azoïque par le groupement imine, il s'agit alors des réactifs du type azométhine. Les mêmes règles, quant à la place des fonctions phénoliques et des fonctions azotées valent dans l'un et l'autre cas.

On obtient de tels composés en condensant par exemple les acides H ou K avec l'aldéhyde salicylique:



Le réactif de KORENMAN s'obtient en mélangeant 1 volume de solution alcoolique à 5% d'aldéhyde salicylique avec 13 volumes d'une solution aqueuse d'acide H ou d'acide K à 1%. À 2.5 ml d'une solution aqueuse contenant de l'acide borique, ajouter 2 ml d'acide acétique *N* et 0.5 ml du réactif précédent: une coloration jaune intense apparaît, alors que le témoin obtenu dans des conditions identiques, mais sans addition d'acide borique, reste coloré en jaune pâle. A remarquer que la base de Schiff obtenue par condensation de l'acide anthranilique avec l'aldéhyde salicylique donne également une réaction colorée jaune avec le bore, mais la sensibilité en ce cas est faible et la dilution limite est de 1/10,000 seulement (KORENMAN[2,3]).

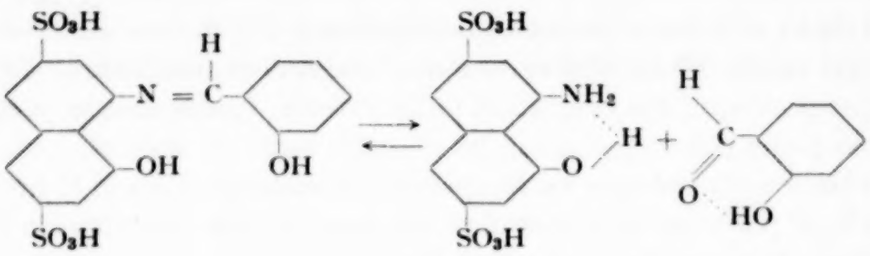


KOULBERG ET BADEVEVA[5] ont synthétisé et isolé le réactif de KORENMAN et abouti aux composés purs résultant de la combinaison des acides H ou K avec l'aldéhyde salicylique*. Le mécanisme de la réaction colorée des azométhines est selon ces auteurs différent de celui de la réaction que donnent les réactifs à groupement azoïque.

* Que l'on appellera pour simplifier Azométhine H ou K.

Alors que l'acide borique provoque un virage de la coloration des réactifs azoïques, en revanche il ne fait qu'accentuer la coloration initiale des azométhines.

Ainsi en solution aqueuse l'azométhine H par exemple se dissocierait selon le schéma:



Or, en solution aqueuse, seule l'azométhine H est colorée en jaune, alors que l'acide H et l'aldéhyde salicylique sont pratiquement incolores. En l'absence d'acide borique ces deux produits ne se combineraient l'un à l'autre que très lentement par suite de la position des groupements fonctionnels en *ortho*, et de la nécessité de la rupture des liaisons hydrogène de l'acide H et de l'aldéhyde salicylique. En présence d'acide borique, celui-ci formant facilement des esters avec les fonctions phénoliques, les groupements $-NH_2$ et $-CHO$ se trouvent libérés et pourraient ainsi se combiner entre eux plus aisément. En définitive, l'acide borique agirait comme un catalyseur qui permettrait à l'équilibre ci-dessus décrit, de se déplacer de droite à gauche, et par suite de condenser l'azométhine, seule substance colorée.

En résumé, les réactifs en question sont des colorants résultant de la combinaison des acides amino-naphtoldisulfoniques avec des polyphénols par l'intermédiaire d'une fonction diazotée, ou avec des aldéhydes comportant un groupement phénolique par l'intermédiaire d'une fonction iminée. Plus particulièrement, ont été retenus par les auteurs soviétiques[4,6] les acides H et K combinés avec les substances que mentionne le Tableau I ci-après; la réaction est un virage du jaune ou du jaune orangé au rouge ou rouge violet pour les colorants azoïques, et une accentuation de la coloration du jaune au jaune plus foncé pour les colorants azométhines. Exemples:

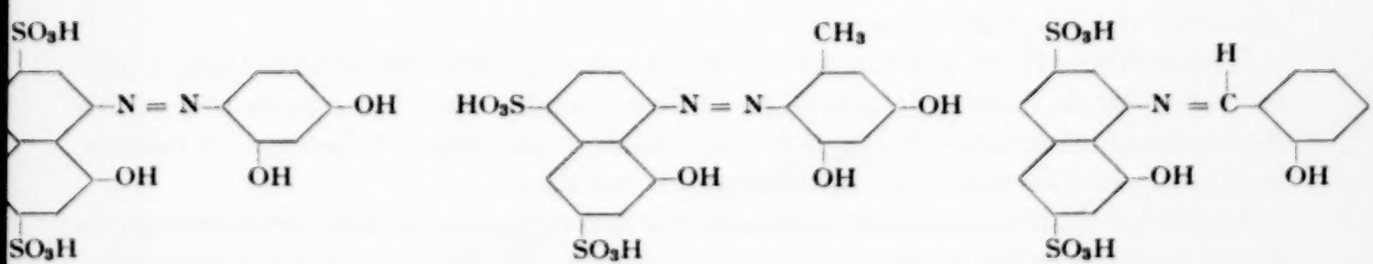


TABLEAU I

Azoïques		*Azométhines*
Acide H et résorcine	Acide K et résorcine	Acide H et aldéhyde salicylique
Acide H et orcine	Acide K et orcine	Acide K et aldéhyde salicylique
Acide H et phloroglucine		
Acide H et pyrogallol		
Acide H et β-naphtol		

MICRODOSAGE DU BORE À L'AIDE DES RÉACTIFS DU TYPE AZOMÉTHINE

L'étude des réactifs de ce groupe résulte de la technique semi-quantitative de KORENMAN[2,3].

À 2.5 ml de la solution neutre de bore à étudier, ajouter 2 ml d'acide acétique *N* et 0.5 ml d'un réactif formé d'un volume de solution alcoolique à 5% d'aldéhyde salicylique et de 13 volumes d'une solution aqueuse à 1% d'acide amino-8-naphtol-1-disulfonique-3,6 (acide H) ou d'acide amino-8-naphtol-1-disulfonique-3,5 (acide K). L'acide borique provoque une coloration jaune intense, l'essai témoin exempt de bore étant coloré en jaune pâle.

La même réaction est obtenue en remplaçant le mélange d'acide H (ou K) et d'aldéhyde salicylique par le produit cristallisé résultant de leur combinaison (azométhine H ou azométhine K) selon KOULBERG ET BADEVEVA[5].

On s'est attaché partant de là, à étudier ces réactions dans le domaine quantitatif. À titre d'indication, des quatre étudiés, le réactif à l'azométhine H présente l'intérêt le plus grand.

Matériel utilisé

Il est fait usage de matériel en silice. Les mesures photométriques sont faites au moyen du spectrophotomètre Jean et Constant.

Réactif à l'azométhine H

*Synthèse de l'azométhine H**

Dissoudre 18 g d'acide H dans un litre d'eau distillée. Tièdir pour faciliter la dissolution. Filtrer. Neutraliser en versant goutte à goutte une solution d'hydroxyde de potassium à 20% jusqu'à virage au Rouge Congo (essai à la touche). Puis réacidifier légèrement en versant goutte à goutte de l'acide chlorhydrique au demi jusqu'à acidification au Rouge Congo (essai à la touche avec virage au bleu très franc). Ajouter un excès de 15 ml d'acide environ (pour avoir un pH de 1.5–3.0). Placer la solution sous un agitateur mécanique et verser goutte à goutte 20 g d'aldéhyde salicylique fraîchement distillé. Agiter énergiquement pendant une heure. Laisser déposer le fin précipité orangé d'azométhine H pendant une nuit. Filtrer sur entonnoir de Büchner. Laver plusieurs fois à l'alcool éthylique, puis à l'éther. Sécher à l'étuve (90–105°) jusqu'à poids constant.

L'azométhine H est une poudre légère d'un orangé clair; elle se décompose à 300° en dégageant de l'aldéhyde salicylique. Elle est soluble dans l'eau, assez peu soluble dans l'alcool méthylique ou éthylique, et insoluble dans l'éther, le benzène, le toluène, le chloroforme, l'acétone, le tétrachlorure de carbone.

Le produit étant légèrement hygroscopique doit être conservé sitôt après étuvage en flacon soigneusement bouché placé lui-même si possible dans une cage à dessiccation.

Mode opératoire

Réactifs

Acide sulfurique ($d = 1.83$) dilué au cinquième (1 : 4) avec de l'eau distillée; Solution d'acétate d'ammonium à 500 g/l; Acide acétique cristallisable et Ammoniaque pure ($d = 0.925$).

* Cette technique indiquée par KOULBERG ET BADEVEVA[5] a été revue par nous sur certains points de détail. La synthèse de l'azométhine K s'effectue selon une technique en tout point identique en remplaçant l'acide H par de l'acide K.

Réactif à l'azométhine H

Azométhine H*, 6 g; Acide ascorbique, 20 g; Eau distillée q.s.p., 1 l.

Liqueur titrée d'acide borique à 10 µg de bore par ml

Peser 5.7135 g d'acide borique cristallisé, séché au dessiccateur à acide sulfurique. Dissoudre le produit dans de l'eau distillée et compléter à 1 l en fiole jaugée avec de l'eau distillée. Diluer au centième la solution précédente avec de l'eau distillée en s'aidant d'une fiole jaugée.

1 ml de cette dernière solution contient 10 µg de bore.

Eau distillée

Peut être obtenue au moyen d'un alambic en cuivre étamé, mais l'emploi d'un appareil distillatoire en silice est cependant plus recommandable. L'eau épurée par passage de l'eau ordinaire sur résines anionique et cationique est à proscrire formellement.

Courbe d'étalonnage

Dans une série de béchers** de 100 ml, introduire successivement: 0, 1, 2, 3 . . . 7–8 ml de liqueur titrée d'acide borique contenant 10 µg de bore par ml, 1.6 ml d'acide sulfurique ($d = 1.83$) dilué au cinquième*** et 10 ml de solution d'acétate d'ammonium à 500 g/l. Ajuster le pH à 5.20 (contrôle à l'électrode de verre) au moyen d'acide acétique ou d'ammoniaque au demi. Transvaser en fioles jaugées de 100 ml. Rincer les béchers avec le minimum d'eau distillée (quelques ml). Ajouter 10 ml+ de réactif à l'azométhine H. Compléter à 100 ml avec de l'eau distillée. Agiter et laisser la coloration se développer à l'obscurité, à 20° ± 5°, pendant 18 h.

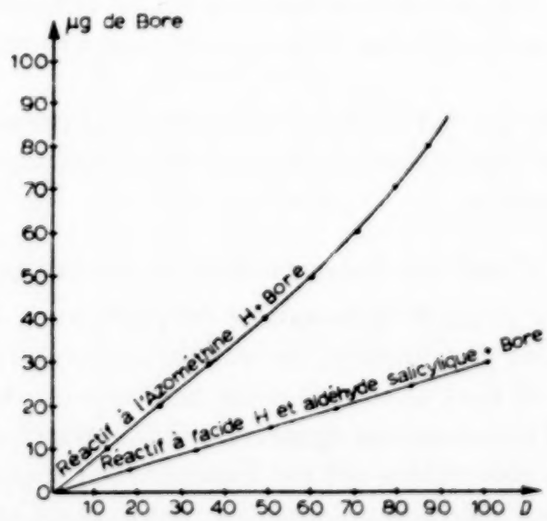


Fig. 1. Courbes d'étalonnage obtenues avec le réactif à l'azométhine H et avec le réactif à l'acide H et aldéhyde salicylique.

* L'azométhine H doit être pesé très exactement.
** Pour toutes les opérations effectuées à froid du matériel en pyrex peut être utilisé. L'emploi de matériel en silice reste cependant plus recommandable.
*** L'addition d'acide sulfurique au cinquième n'est pas indispensable.
+ À mesurer très exactement.

Au bout de ce temps, les colorations des différents termes de la gamme d'étalonnage sont mesurées par rapport à celle du terme zéro, à $\lambda = 415$ mμ.

Les résultats obtenus sont ceux représentés dans la Fig. 1*. La courbe obtenue est pratiquement une droite entre 0 et 50 μg de bore.

Dosage

La solution neutre contenant l'acide borique à doser (entre 0 et 100 μg de bore) est traitée selon la technique de la gamme d'étalonnage.

Discussion

Étude qualitative du réactif

Le réactif a été préparé selon les deux formules suivantes: *Réactif A*: azométhine H, 0.6 g et eau distillée q.s.p., 100 ml; *Réactif B*: azométhine H, 0.6 g, acide ascorbique, 2 g et eau distillée q.s.p., 100 ml.

Dans des fioles jaugées de 100 ml sont distribués successivement: 30 ml de solution titrée d'acide borique (1 ml = 1 μg de bore), 1.6 ml d'acide sulfurique ($d = 1.83$) dilué au cinquième, 10 ml de solution d'acétate d'ammonium à 500 g/l, 10 ml de Réactif A ou B et eau distillée q.s.p. 100 ml. Des témoins correspondants sans bore ont été préparés.

Un essai et un témoin de chacune des séries A et B a été placé pendant 24 h à l'obscurité, l'autre essai ou témoin de chaque série restant exposé pendant le même temps à la lumière du jour. Des observations faites à des intervalles de temps réguliers montrent que dans tous les essais avec bore une coloration jaune se développe assez lentement pour atteindre son complet développement au bout de 6 h environ, tandis que les témoins sans bore restent pratiquement incolores. Au bout de 24 h les essais et témoins A (sans acide ascorbique) laissés à la lumière du jour présentent un très léger brunissement par rapport aux mêmes essais ou témoins laissés à l'obscurité; par contre dans les essais ou témoins B (avec acide ascorbique) aucun brunissement n'apparaît.

Ces résultats montrent que le réactif à l'azométhine H préparé en présence d'acide ascorbique (réactif B) est plus stable à l'air et que les colorations doivent de préférence être développées à l'obscurité.

Influence de la longueur d'onde sur l'absorption de la lumière incidente

Deux essais contenant 30 μg de bore ont été préparés avec du réactif B en suivant la même technique. Avant de compléter les volumes à 100 ml, les pH des deux essais ont été réglés à pH 5.0 et 6.15 avec de l'acide acétique ou de l'ammoniaque. Deux témoins correspondants sans bore ont également été préparés. Après 18 h de développement à l'obscurité les colorations ont été mesurées par rapport à de l'eau distillée.

La Fig. 2 représente les résultats obtenus. Le maximum d'absorption se situe donc vers $\lambda = 415$ mμ à pH 5.0.

Influence du pH sur l'intensité de la coloration

Une série d'essais contenant 30 μg de bore et des témoins correspondants exempts de bore sont amenés à différents pH par introduction d'acide acétique ou d'ammo-

* Avec cuves de 2 cm; la sensibilité du spectrophotomètre étant réglée pour correspondre à une tare optique de 60.

niaque (contrôle à l'électrode de verre). Après 18 h de développement à l'obscurité, les colorations des différents essais ont été mesurées par rapport à leurs témoins correspondants, à $\lambda = 415$ mμ.

Selon les résultats obtenus qui sont représentés sur la Fig. 3, l'intensité de la coloration est maximale vers pH 5.2, et elle reste pratiquement constante entre pH 4.8 et 5.6.

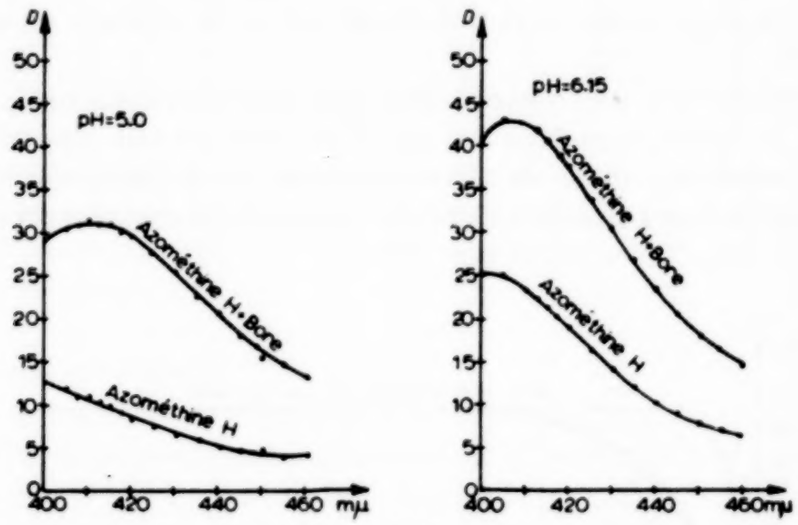


Fig. 2. Courbes d'absorption du réactif à l'azométhine H et du complexe coloré azométhine H + bore en fonction de la longueur d'onde, à pH 5.0 et 6.15

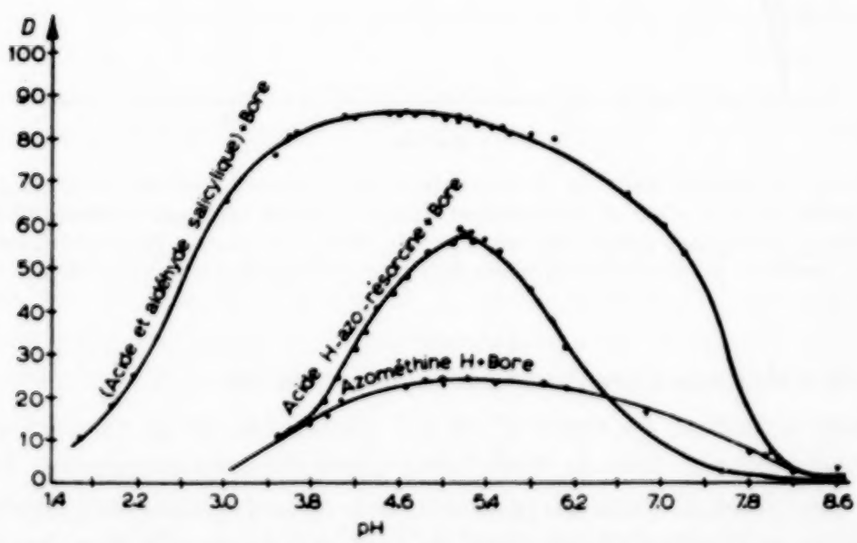


Fig. 3. Influence du pH sur l'intensité de la coloration du complexe coloré azométhine H + bore; du complexe coloré obtenu avec le réactif à l'acide H et aldéhyde salicylique + bore; et du complexe coloré obtenu avec le réactif à l'acide H –azo–résorcine + bore.

À remarquer que la coloration jaune pâle des témoins augmente progressivement quant le pH s'élève. Dans la zône de pH 8.0–9.0 la coloration jaune des témoins est presque aussi intense que celle des essais.

Vitesse de développement de la coloration

Une série d'essais contenant 30 μg de bore et de témoins sans bore a été préparée selon la technique précédente, le pH final étant de 5.2. Les essais et témoins sont placés à l'obscurité, la température étant de 20° ± 5°, et des mesures de coloration des différents essais par rapport à leurs témoins sont faites à des intervalles de temps qui ont été notés.

Les résultats obtenus représentés sur la Fig. 4 montrent que le développement de la coloration due au bore est rapide pendant les cinq premières heures, puis se ralentit considérablement pour tendre vers une limite qui n'est atteinte qu'après plusieurs jours de contact.

Les mesures photométriques doivent donc être effectuées après un temps déterminé qui doit rester le même dans tous les cas. L'on peut en fait effectuer les mesures après 18 h de repos, la vitesse de développement de la coloration devenant alors suffisamment faible pour permettre d'obtenir des résultats constants et reproductibles.

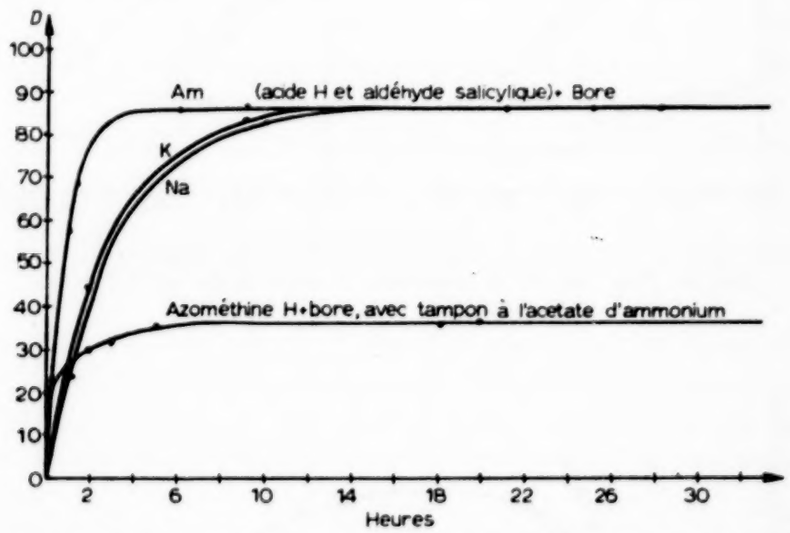


Fig. 4. Vitesse de développement de la coloration du complexe coloré azométhine H + bore, à 20° ± 5°, en présence d'acétate d'ammonium utilisé comme tampon. Vitesse de développement de la coloration du complexe coloré obtenu avec le réactif à l'acide H et aldéhyde salicylique + bore en présence de tampon sodique, potassique et ammonique.

Influence de la température sur l'intensité de la coloration

L'expérience a montré qu'entre 5° et 25° l'intensité de la coloration obtenue en présence d'une quantité fixe de bore reste pratiquement constante. Par chauffage (vers 50°) la coloration obtenue en présence de bore augmente considérablement, mais celle des témoins exempts de bore varie de la même façon. De plus, un brunissement de fond se superpose alors à la coloration jaune normale, de sorte que la différence de coloration entre l'essai et le témoin est finalement plus faible. En définitive, les colorations peuvent être commodément développées à 20° ± 5°.

Influence de la concentration du réactif en azométhine H

L'intensité de la coloration obtenue dépend étroitement de la quantité d'azométhine H présente dans le milieu réactionnel, ainsi que le montrent les résultats du

Tableau II, obtenus en présence d'une quantité constante de bore, soit 30 μg, et d'un même volume de réactif dont la concentration en azométhine H était variable. Dans tous les cas le pH est égal à 5.2.

TABLEAU II

Essai No.	*Concentration du réactif en azométhine H (g/l)*	*Déviations photométriques*	*pH essai*	*pH témoin*
1	3	15	5.23	5.23
2	4	23	5.25	5.25
3	5	29	5.25	5.25
4	6	35	5.25	5.25
5	7	39.5	5.25	5.25

On a donc intérêt à utiliser un réactif aussi concentré que possible en azométhine H. Mais l'expérience ayant montré qu'il est assez difficile de dissoudre à froid 7 g d'azométhine H par litre, c'est donc la composition du réactif indiquée dans mode opératoire qui a été adoptée.

Ordre d'introduction des réactifs

Cet ordre a une influence assez marquée sur la reproductibilité des résultats. En effet, une certaine dispersion dans les résultats a été observée lors d'essais dans lesquels le réactif avait d'abord été introduit, puis où le pH avait été ajusté par tâtonnement avec de l'acide acétique ou de l'ammoniaque au demi. La quantité d'ammoniaque ajoutée ayant été trop forte en certains cas et la valeur visée du pH dépassée, il a fallu réacidifier partiellement par l'acide acétique. Dans de telles conditions l'addition d'ammoniaque augmente visiblement l'intensité de la coloration jaune des témoins, laquelle n'est sans doute que partiellement diminuée quand l'on réacidifie par de l'acide acétique.

Les résultats sont au contraire très réguliers et reproductibles quand le réactif à l'azométhine H est ajouté en dernier après fixation du pH.

Influence des éléments étrangers

Les éléments suivants: Sb, As, Ba, Bi, Cd, Ca, Cs, Co, K, Li, Mg, Mn, Nd, Ni, Nb, Pb, Re, Se, Na, Sr, Ta, Te, Tl, Th, W, U et Zn, ainsi que NO_3^-, $P_2O_5^{-3}$, Cl^-, F^-, SO_3^{-2}, $C_2O_4^{-2}$ et WO_3, ne donnent aucune coloration avec le réactif.

Na^+ et K^+ ralentissent le développement de la coloration. Sn(II), Te et Hg(II)

TABLEAU III

Elément gênant	*Poids de l'élément gênant qui donne avec le réactif à l'azométhine H la même coloration que 1 µg de bore*
Mo (MoO_3)	625
Zr	25
Al	2.1
Be	0.5
Ti	11.1
V(IV)	2.5
V(V)	2.5
Cu	4.5
Cr	11.1

donnent un précipité blanc. Cu et Cr donnent une coloration jaune brun. Fe(II), Fe(III), ainsi que l'ion nitrite NO_2^- donnent un fort brunissement. Les sulfites empêchent la coloration de se développer. Les molybdates donnent une coloration jaune très faible s'ils sont en quantité trop importante. Enfin Al, Be, Ti, Zr, V(IV), V(V) et Ga donnent une coloration jaune très intense.

Dans le Tableau III on a reproduit le poids des différents éléments gênants qui donne avec le réactif à l'azométhine H la même coloration que 1 μg de bore.

Résumé

Les paramètres expérimentaux de la réaction de l'azométhine H avec le bore, en milieu aqueux acide, ont été précisés: introduction d'acide ascorbique comme anti-oxygène, domaine de pH, longueur d'onde optimale, influence de la température; le complet développement n'est atteint qu'après plusieurs jours de contact et les mesures seront faites après écoulement d'un temps déterminé convenablement.

Du point de vue pratique, l'acétate d'ammonium étant employé comme tampon, les mesures photométriques peuvent être effectuées après repos de 18 h à l'obscurité, la température ambiante restant comprise entre 15° et 25°. Le pH optimum de 5.2 peut en fait varier entre pH 4.8 et 5.6. Longueur d'onde optimale pour les mesures: $\lambda = 415$ mμ.

L'intensité de la coloration dépend des quantités présentes de bore et d'azométhine H, ce qui oblige pour les mesures à employer des quantités exactement mesurées d'un réactif dont la composition optimale a été déterminée.

La sensibilité du nouveau réactif a été trouvée voisine de 0.01 μg de bore par ml, c'est-à-dire équivalente à celles d'autres réactifs plus classiques.

Quelques éléments, dont la liste a été indiquée, peuvent gêner et doivent être soigneusement éliminés s'ils sont présents.

Réactif à l'azométhine K

L'étude de ce réactif a montré que l'azométhine K obtenu en remplaçant l'acide H par de l'acide K, a des propriétés absolument analogues à celles de l'azométhine H.

Tout ce qui a été dit précédemment est donc entièrement valable lorsqu'il est fait usage de l'azométhine K; toutefois la longueur d'onde optimale pour les mesures (absorption maximale) a été trouvée à $\lambda = 417.5$ mμ au lieu de 415 mμ.

Réactif à l'acide H et aldéhyde salicylique

Le réactif indiqué par KORENMAN[2,3] et dont la composition a été indiquée antérieurement, n'est en fait pas stable à l'air, il se produit un brunissement assez rapide, surtout à la lumière du jour. Pour empêcher ce brunissement il est nécessaire d'ajouter un réducteur. Là encore l'acide ascorbique s'est montré le réducteur le mieux approprié.

Réactifs particuliers

Solution A (à préparer extemporanément): acide amino-8-naphtol-1-disulfonique-3,6 (acide H), 1 g; acide ascorbique, 2 g; eau distillée q.s.p., 100 ml.

Solution B: aldéhyde salicylique (fraîchement distillé), 5 g; alcool éthylique à 95° q.s.p., 100 ml.

Le réactif s'obtient en mélangeant au moment de l'emploi 13 volumes de solution A et 1 volume de solution B, soit 91 ml de solution A et 7 ml de solution B.

Par ailleurs, les mêmes réactifs que ceux déjà indiqués antérieurement.

Courbe d'étalonnage

Dans une série de béchers de 50 ml, introduire successivement: 0, 1, 2, 3. . . . 7–8 ml de liqueur titrée d'acide borique contenant 10 μg de bore par ml et 10 ml de solution d'acétate d'ammonium à 500 g/l. Ajuster le pH à 4.60 avec de l'acide acétique (ou de l'ammoniaque) au demi (contrôle à l'électrode de verre). Transvaser en fioles jaugées de 50 ml. Rincer les béchers avec le minimum d'eau distillée (quelques ml). Ajouter 5 ml de réactif à l'acide H et aldéhyde salicylique. Compléter à 50 ml avec de l'eau distillée. Agiter et laisser la coloration se développer à l'obscurité, à 20° ± 5°, pendant 18 h.

Au bout de ce temps, les colorations des différents termes de la gamme d'étalonnage sont mesurées par rapport à celle du terme zéro, à $\lambda = 415$ mμ. La courbe d'étalonnage obtenue est celle représentée dans la Fig. 1*.

Dosage

La solution neutre contenant l'acide borique à doser (entre 0 et 50 μg de bore) est traitée selon la technique de la gamme d'étalonnage.

Discussion

Étude qualitative du réactif: Le réactif à l'acide H + aldéhyde salicylique donne également, en solution aqueuse acide, une coloration jaune intense avec le bore, mais les témoins correspondants sans bore sont nettement plus colorés en jaune que ceux obtenus avec le réactif à l'azométhine H étudié ci-dessus. Malgré l'addition d'acide ascorbique la stabilité à l'air du réactif est un peu moins bonne que celle du réactif à l'azométhine H, un très léger brunissement de fond peut se produire si les essais avec ou sans bore restent exposés trop longtemps à une lumière trop vive. Il faut donc effectuer les mesures assez rapidement (en moins d'une heure) dès que les essais sont sortis de l'obscurité.

La longueur d'onde optimale pour les mesures: se situe, comme dans le cas du réactif à l'azométhine H, à $\lambda = 415$ mμ.

Influence du pH sur l'intensité de la coloration due au bore: Celle-ci a été déterminée en distribuant dans une série de béchers de 50 ml: 2.5 ml de solution titrée de bore, dont 1 ml contient 10 μg de bore, 10 ml de solution d'acétate d'ammonium à 500 g/l et une quantité variable d'acide acétique ou d'ammoniaque pour amener le pH de chacun des termes à une valeur comprise entre pH 1.4 et 8.6.

Après transvasement en fioles jaugées et rinçage des béchers avec quelques ml d'eau distillée, addition de 5 ml de réactif à l'acide H + aldéhyde salicylique. Après quoi, le volume de chaque terme est complété à 50 ml avec de l'eau distillée. Agitation. Par ailleurs des témoins correspondants exempts de bore ont été établis parallèlement. Après 18 h de développement à l'obscurité (température ambiante: 20° ± 5°), la coloration des différents essais a été mesurée par rapport à celle des témoins corres-

* En cuves de 2 cm également, et avec le même réglage de la sensibilité du spectrophotomètre que précédemment.

pondants à $\lambda = 415$ mμ. Les résultats obtenus sont reproduits dans la Fig. 3.

La déviation photométrique maximale est donc obtenue vers pH 4.60; toutefois entre pH 4.10 et 5.15, les résultats peuvent être considérés comme constants.

Vitesse de développement de la coloration: La cinétique de la réaction colorée est la même que dans le cas du réactif à l'azométhine H. L'acétate d'ammonium étant utilisé comme tampon, la coloration peut être mesurée pratiquement après repos de 18 h; mais s'il est fait usage de l'acétate de sodium ou de potassium, la coloration est plus longue à se développer, comme le montrent les résultats représentés sur la Fig. 4.

Influence de la température sur l'intensité de la coloration: Entre 0 et 25°, les colorations obtenues en présence d'une quantité fixe de bore peuvent être considérées comme constantes. Pratiquement des résultats très reproductibles sont obtenus en développant les colorations à $20° \pm 5°$.

Influence de la composition du réactif sur l'intensité de la coloration: La quantité de bore en expérience restant constante et le volume ajouté de réactif restant également constant, l'intensité de la coloration obtenue dépend étroitement de la concentration du réactif en acide H et en aldéhyde salicylique; par contre la quantité ajoutée d'acide ascorbique n'a guère d'influence. Il est donc nécessaire de préparer très exactement le réactif et de le conserver identique dans une même série de dosages.

Après 18 h de développement à l'obscurité les résultats obtenus sont alors très reproductibles. Les mesures photométriques doivent être faites assez rapidement, car après une heure d'exposition à la lumière du jour, une baisse déjà sensible de la coloration peut être observée.

Les colorations obtenues avec le réactif à l'acide H et aldéhyde salicylique sont donc moins stables que celles obtenues avec le réactif à l'azométhine H.

Ordre d'introduction des réactifs: Les meilleurs résultats ont encore été obtenus en n'introduisant qu'après établissement du pH approprié le réactif à l'acide H et aldéhyde salicylique.

Influence des éléments étrangers: Mêmes observations que pour le réactif à l'azométhine H.

Conclusion

Le réactif à l'acide H et aldéhyde salicylique a donc des propriétés sensiblement analogues à celles du réactif à l'azométhine H. Il en diffère toutefois sur les points suivants: pH optimal pour les mesures trouvé égal à 4.60, avec résultats pratiquement constants entre pH 4.10 et 5.15, coloration jaune plus intense des témoins et moins bonne stabilité des colorations que de celles obtenues avec l'azométhine H.

Réactif à l'acide K et aldéhyde salicylique

L'étude de ce réactif, obtenu en remplaçant dans le réactif précédent l'acide H par de l'acide K, a montré que les deux réactifs ont des propriétés identiques, à l'exception de la longueur d'onde optimale qui a été trouvée de 417.5 mμ au lieu de 415 mμ.

Autres colorants dérivés de l'acide H

Quelques essais ont également été effectués en remplaçant l'acide H par des colorants dérivés de l'acide H. Les principaux colorants utilisés ont été les suivants:

Noir naphtalène 12 BN (C.I.: 20.470 Acid black 1). Vert noir pour laine J (C.I.: 20.495 Acid Green 20), Bleu diazol 2 B (C.I.: 22.610 — Direct blue 6), Bleu diazol V (C.I.: 23.710 — Direct blue 21), Noir diazol BH (C.I.: 22.590 — Direct blue 2), Bleu pur diazol 4 B (C.I.: 24.400 — Direct blue 15) et Vert para 2 BL(Bayer) (C.I.: 22.230).

En aucun cas il n'est apparu la moindre trace de coloration en présence de bore, même après repos de plusieurs jours. Ceci montre que la réactivité à l'égard du bore des composés ayant la structure de base énoncée par POLUEKTOV ET NIKONOVA[4] cesse de se manifester si la structure moléculaire devient trop compliquée, ou si les diverses positions du noyau naphtalène sont trop encombrées.

En résumé, de tous les réactifs à groupement imine étudiés précédemment seul a été retenu l'azométhine H.

MICRODOSAGE DU BORE EN MILIEU AQUEUX ACIDE À L'AIDE DE RÉACTIFS À GROUPEMENT AZOÏQUE

Parmi les nombreux réactifs indiqués par POLUEKTOV ET NIKONOVA[4] les deux suivants obtenus par diazotation de l'acide H ou de l'acide K avec la résorcine ont été seulement étudiés*.

Réactif à l'acide (azo-1'-dihydroxy-2,4-benzène)-1-hydroxy-8-naphtalène disulfonique-3,6 (acide H-azo-résorcine)

Réactif à l'acide H-azo-résorcine

Colorant, 0.100 g** et eau distillée q.s.p., 1 l. Par ailleurs, les mêmes réactifs que ceux déjà indiqués pour l'étude du réactif à l'azométhine H.

Courbe d'étalonnage

Dans une série de béchers de 100 ml distribuer successivement: 0, 1, 2, 3 . . . 7 ml de solution titrée d'acide borique dont 1 ml contient 10 μg de bore. Puis dans chaque bécher ajouter: 1.6 ml d'acide sulfurique (d = 1.83) dilué au cinquième*** et 10 ml de solution d'acétate d'ammonium à 500 g/l.

Régler le pH à 5.20 par de l'ammoniaque ou de l'acide acétique (contrôle à l'électrode de verre). Transvaser dans une série de fioles jaugées de 100 ml. Rincer les béchers avec le minimum d'eau distillée (quelques ml). Ajouter 10 ml de réactif à l'acide H-azo-résorcine+. Compléter à 100 ml avec de l'eau distillée. Agiter. Après repos de 72 h à l'obscurité, (la température restant comprise entre 16° et 20°), la coloration des différents termes de la gamme est mesurée par rapport à celle du terme zéro exempt de bore.

Les résultats obtenus sont représentés dans la Fig. 5++. La courbe ne suit donc pas la loi de LAMBERT-BEER, et il y aurait intérêt dans ces conditions à effectuer les mesures en colorimétrie différentielle.

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* Ces deux colorants, ainsi que ceux dérivés de l'acide H dont il a été fait mention, nous ont été fournis gracieusement par la Société Francolor, à qui vont nos remerciements.

** Le colorant doit être pesé très exactement.

*** L'addition d'acide sulfurique dilué au cinquième n'est pas indispensable.

+ Le réactif doit être mesuré très exactement.

++ En cuves de 2 cm, et avec même réglage de la sensibilité du spectrophotomètre que précédemment.

Dosage

La solution neutre contenant l'acide borique à doser (0 à 50 μg de bore) est traitée selon la technique de la gamme d'étalonnage.

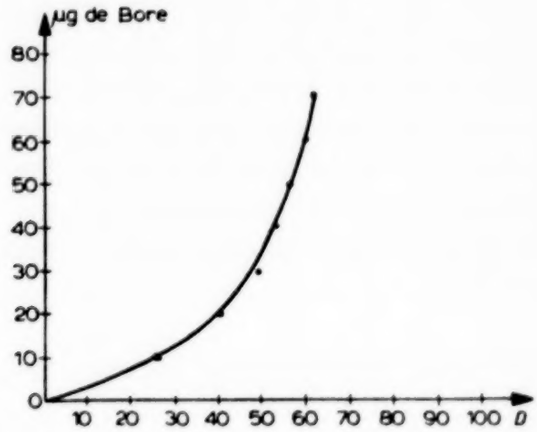

Fig. 5. Courbe d'étalonnage obtenue avec le réactif à l'acide H-azo-résorcine.

Discussion

Étude qualitative et choix du réactif: Au moyen des deux réactifs suivants: *Réactif A:* Colorant, 0.100 g et eau distillée q.s.p., 1 l; *Réactif B:* Colorant, 0.100 g, acide ascorbique, 20 g et eau distillée q.s.p., 1 l les essais suivants ont été effectués.

Dans des fioles jaugées de 100 ml verser: 5 ml de solution titrée d'acide borique, dont 1 ml contient 10 μg de bore, 1.6 ml d'acide sulfurique (d = 1.83) dilué au cinquième, 10 ml de solution d'acétate d'ammonium à 500 g/l et 10 ml de réactif A ou B. Compléter à 100 ml avec de l'eau distillée. Agiter. Préparer des témoins correspondants exempts de bore.

Certains des essais et des témoins de chaque série sont laissés à l'obscurité et les autres sont maintenus à la lumière du jour.

Il est observé que tous les essais avec bore, d'abord colorés en jaune orangé virent peu à peu au rouge orangé, et le complet développement de la coloration n'est atteint qu'après plusieurs heures (65 h environ); elle reste ensuite stable pendant plusieurs jours. Les témoins exempts de bore restent colorés en jaune orangé.

Dans tous les essais avec bore et dans les témoins sans bore laissés à la lumière du jour, il apparaît peu à peu un très léger brunissement.

La coloration rouge des essais avec bore ayant reçu une addition d'acide ascorbique (réactif B) se développe progressivement pour atteindre son maximum d'intensité au bout de 45 h environ, mais diminue ensuite progressivement, et après 5 ou 6 jours, les essais et témoins préparés avec le réactif B sont très nettement décolorés. L'addition d'acide ascorbique n'est donc pas bénéfique.

Il ressort de ces essais que les meilleurs résultats sont obtenus en utilisant le réactif A, et en laissant les colorations se développer à l'obscurité. Ce réactif a été adopté définitivement.

Absorption de la lumière incidente en fonction de la longueur d'onde par le colorant et le complexe coloré (colorant + bore). Un essai et un témoin exempt de bore sont maintenus pendant 65 h à l'obscurité; puis la coloration de l'essai et celle du témoin sont mesurées par rapport à de l'eau distillée, à différentes longueurs d'onde. Les

résultats obtenus sont représentés sur la Fig. 6. Le complexe coloré (en présence de bore) présente un maximum d'absorption à $\lambda = 515$ mμ environ, et pour le colorant seul le maximum se situe à $\lambda = 480$ mμ environ. Si l'on mesure la variation de densité optique du complexe coloré avec bore par rapport à celle du colorant seul, le maximum d'absorption, donc la sensibilité maximale pour les mesures, se situe à $\lambda = 515$ mμ.

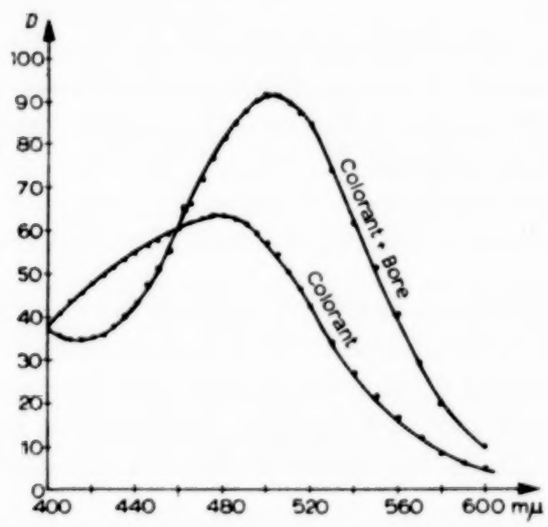

Fig. 6. Courbe d'absorption du colorant (acide H-azo-résorcine) et du complexe coloré avec le bore (colorant + bore).

Influence du pH sur l'intensité de la coloration due au bore: Dans des essais contenant une quantité constante de bore (soit 50 μg), on a fait varier progressivement le pH d'un terme à l'autre par addition de quantités variables d'acide acétique ou d'ammoniaque. Des témoins de même pH exempts de bore sont préparés parallèlement.

Après repos de 65 h à l'obscurité la densité optique des essais est mesurée par rapport à celle des témoins sans bore correspondants. Les résultats obtenus, représentés sur la Fig. 3, montrent que l'intensité de la coloration obtenue avec le bore est très sensible à l'influence du pH, et que le maximum d'intensité est obtenu à pH 5.20 environ (pratiquement les résultats restent constants entre pH 5.15 et 5.25).

Influence de la température et de la durée sur le développement de la coloration due au bore: Le développement de la réaction colorée de l'acide borique avec le réactif étudié est accéléré par chauffage et l'intensité de la coloration obtenue est fonction de la température à laquelle elle a été développée. Le Tableau IV résume les observations relevées.

À la température de 16–20°, la coloration se développe lentement pour atteindre son maximum d'intensité après 65 h; il faut 85 h à la température de 12 à 15°. L'intensité de la coloration reste alors stable pendant plusieurs heures, ou même plusieurs jours.

À chaud, la coloration se développe beaucoup plus vite, mais elle n'est ni stable, ni constante en intensité. Ainsi, dès 40°, les témoins se décolorent progressivement, ainsi que les essais contenant du bore. Les résultats ne sont ni constants, ni réguliers. Il est donc nécessaire que la réaction soit faite à froid, et à température constante, et que les mesures soient effectuées au bout d'un temps déterminé, qui doit rester le même dans tous les cas.

Le plus aisé est de laisser la coloration se développer à une température de 16–20°, et d'effectuer en ce cas les mesures photométriques après 72 h de repos à l'obscurité, l'intensité maximale de la coloration étant alors pratiquement atteinte.

TABLEAU IV

Essai	*Température de développement de la coloration*	*pH*	*Déviations photométriques obtenues après développement de la coloration pendant:*											
			2 h	*5 h*	*8 h*	*18 h*	*24 h*	*26 h*	*42 h*	*51 h*	*65 h*	*72 h*	*88 h*	*150 h*
A	12–15°	5.20				25		37	46	51	56.5	57	58.5	58.5
B	16–20°	5.20				30.5		41.5	49.5	53.5	56	56	56	56
C	40–42°	5.20		32	40	48	41	37.5	28	25.5	23.5			
D	64–65°	5.20		35	28									
E	95–100°	5.20	26	25										

Influence de la concentration du réactif en colorant sur l'intensité de la coloration obtenue avec le bore: Dans le mode opératoire déjà indiqué antérieurement, on a remplacé les 10 ml de réactif contenant 0.100 g de colorant par litre, par 10 ml de réactif contenant 0.200 g ou 0.300 g de colorant par litre. Les résultats indiqués dans le Tableau V montrent que l'intensité de la coloration dépend étroitement de la quantité de colorant introduite.

TABLEAU V

Essai	*Quantité présente de bore dans les essais*	*Concentration du réactif en colorant (g/l)*	*Déviations photométriques*	*pH essai*	*pH témoin*
1	50 µg	0.100	28	5.20	5.20
2	50 µg	0.200	53.5	5.20	5.20
3	50 µg	0.300	74	5.20	5.20

Du point de vue pratique, l'expérience montrant que les témoins No. 2 et 3, préparés avec du réactif contenant 0.200 g ou 0.300 g de colorant par litre, sont très fortement colorés en jaune, il a été jugé préférable de retenir seulement le réactif déjà utilisé et contenant 0.100 g de colorant par litre.

Influence des éléments étrangers: Les éléments Sb, As, Ba, Bi, Cd, Ca, Ce, Cs, Di, Li, Mg, Mn, Nd, Ni, Nb, Pb, K, Re, Se, Na, Sr, Ta, Te, Tl, W, Zn, ainsi que NO_3^-, $P_2O_5^{-3}$, Cl^-, F^-, SO_3^{-2}, $C_2O_4^{-2}$, WO_3 ne donnent pas de coloration avec le réactif. Na et K ralentissent le développement de la coloration. Co, Fe, Mo, U, Hg, Au,

TABLEAU VI

Elément gênant	*Poids de l'élément gênant qui donne avec le réactif la même coloration que 1 µg de bore (µg)*
Cr	5,000
Cu	1,660
Al	1,250
Be	715
Ti	1,660
V(IV)	455
V(V)	625

Pt, SO_2 et NO_2, entraînent un brunissement plus ou moins intense du réactif. Sn, Te et Hg(II) donnent un précipité blanc. Be, Cr, Cu, Al, Th, Ti, V et Zr donnent une coloration rouge plus ou moins intense. La correspondance en bore de chacun de ces éléments gênants est indiquée dans le Tableau VI.

Résumé

Le colorant azoïque constitué par l'acide H et la résorcine (acide (azo-1'-dihydroxy-2,4-benzène)-1-hydroxy-8-naphtalène disulfonique-3,6) donne avec le bore, en milieu aqueux acide, une coloration rouge qui ne se développe que très lentement. À la température ambiante (16–20°), le complet développement n'est obtenu qu'au bout de 65 h, la coloration reste alors stable pendant plusieurs jours.

L'intensité de la coloration obtenue est très sensible à l'influence de la température, du pH et de la concentration du réactif en colorant. Par chauffage, la vitesse de développement peut être augmentée, mais les résultats obtenus ne sont ni réguliers, ni stables.

Les mesures doivent être effectuées dans des conditions toujours identiques quant à la durée et à la température de développement de la coloration, au pH, et à la concentration du réactif.

Les conditions optimales sont les suivantes quand on utilise de l'acétate d'ammonium comme tampon : Développement à l'obscurité, à la température de 16–20°, pendant 72 h ; pH optimal : 5.20, les résultats étant pratiquement identiques pour des valeurs du pH comprises entre 5.15 et 5.25 ; longueur d'onde optimale pour les mesures : 515 mμ ; la courbe d'étalonnage n'est pas une droite ; sensibilité : 0.01 μg de bore par ml environ ; de nombreux ions gênent et doivent être éliminés s'ils sont présents.

Réactif à l'azoïque de l'acide K et de la résorcine (acide (azo-1'-dihydroxy-2,4-benzène)-1-hydroxy-8-naphtalène disulfonique-3,5)

La structure de ce composé a déjà été indiquée dans le Tableau I. L'étude de ce réactif a montré qu'il présente des propriétés pratiquement analogues à celles du précédent sous réserve des quelques points de détail suivants : Longueur d'onde optimale pour les mesures (sensibilité maximale) observée à 520 mμ ; influence encore plus marquée du pH sur l'intensité de la coloration (pH optimal ; 5.20 avec résultats pratiquement identiques entre pH 5.15 et 5.25 seulement) ; développement beaucoup plus lent de la coloration, dont le complet développement n'a été obtenu qu'après repos de 325 h à la température de 16–20° ; sensibilité analogue à l'égard du bore (soit 0.01 μg de bore par ml environ) ; mêmes interférences des éléments étrangers.

Autres colorants

Les autres colorants suivants, bien que n'ayant pas la structure fondamentale énoncée par POLUEKTOV ET NIKONOVA[4] ont néanmoins été expérimentés :

acide amino-2-phénolsulfonique-4 } Acide N,N'-bis[hydroxy-1-(hydroxy-2'-sulfo-5'-phénylazo)-2-sulfo-3-naphtyl-6]urée.
acide amino-2-phénolsulfonique-4 }

amino-2-phénol-sulfonamido-4 } Acide N,N'-bis[hydroxy-1-(hydroxy-2'-sulfo-5'-
amino-2-phénol-sulfamide-4 } phénylazo)-2-sulfo-3-naphtyl-6]urée.

chloro-4-amino-2-phénol } Acide N,N'-bis[hydroxy-1-(hydroxy-2-'sulfo-
chloro-4-amino-2-phénol } 5'-phénylazo)-2-sulfo-3-naphtyl-6]urée.

acide amino-2-phénolsulfonique-4 } Acide dihydroxy-1,8-naphtalène disulfonique--3,6.

acide amino-1-naphtol-2-sulfonique-1,4 } Acide naphtol-1-sulfonique-8.

Bordeaux au chrome solide R (C.I. 14.290 Mordant Red 5).

En aucun cas, aucune coloration n'est apparue en présence de bore, ce qui confirme bien l'hypothèse de POLUEKTOV ET NIKONOVA[4] concernant la structure que doivent avoir les colorants pour donner une réaction colorée avec le bore en milieu aqueux acide.

RÉSUMÉ

Différents réactifs préparés avec des colorants comportant des groupements imine ou azoïque ont été expérimentés en vue du microdosage colorimétrique du bore en milieu aqueux acide. Au total, 19 réactifs ou colorants différents ont ainsi été essayés, dont 6 seulement se sont montrés utilisables, et les conditions d'emploi de ces 6 réactifs ont été étudiées et précisées. Les résultats obtenus montrent que, de tous ces réactifs, le plus pratique et le plus commode d'emploi est de loin celui à l'azométhine H (dérivé de l'acide H et de l'aldéhyde salicylique). La sensibilité de ce réactif à l'égard du bore est équivalente à celle d'autres réactifs classiques, mais il offre sur ceux-ci l'avantage important d'opérer en milieu aqueux. Le réactif n'est cependant pas entièrement spécifique du bore; un certain nombre d'éléments peuvent gêner et doivent être éliminés s'ils sont présents. Le réactif à l'azoïque de l'acide H et de la résorcine présente également un certain intérêt; il est cependant beaucoup moins avantageux que le précédent.

SUMMARY

For the colorimetric microdetermination of boron, 19 dye-stuffs containing imine or azo groups have been examined; only 6 of these were usable and much the best was azomethine-H. This reagent can be used in aqueous media.

ZUSAMMENFASSUNG

Für die colorimetrische Mikrobestimmung von Bor wurden 19 verschiedene Farbstoffe, die Imin- oder Azogruppen enthalten geprüft, von denen sich 6 als brauchbar erwiesen. Keiner ist jedoch dem Azomethin H überlegen.

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DIE BESTIMMUNG VON LITHIUM IN SILIKATISCHEN MINERALIEN (ZINNWALDITKONZENTRAT) MITTELS FLAMMENPHOTOMETRIE

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Bei der direkten flammenphotometrischen Bestimmung von Lithium in Zinnwalditkonzentraten treten Störungen infolge anwesender Begleitelemente wie Si, Fe, Mn, Mg, Al, Na und K auf, deren Kompensation mittels Rahmenlösungen für alle auftretenden Kombinationen zu umfangreich wird. Es erfolgt deshalb eine Abtrennung der Schwer- und Erdalkalimetalle durch einen Anionen-Ionenaustauscher in der Oxalat- und EDTA-Form und eine Auftrennung der Alkalien mittels eines Kationenaustauschers. Im Vergleich dazu wird eine vorherige Abtrennung der Störelemente mit Cadmiumoxyd und basischem Bleicarbonat durchgeführt.

Apparatives

Zur Lithium- und Kalium-Bestimmung diente ein Flammenphotometer No. III der Fa. Zeiss Jena mit einem vorgeschalteten Metallinterferenzfilter Li 67 (671 ± 7 nm) für Lithium und K 76 (768 ± 8 nm) für Kalium. Die Störelementabtrennung erfolgte einmal in einer Kationenaustauschersäule (Durchmesser 10 mm, Höhe 1120 mm, Austauscher: Wofatit KPS 200 der Fa. VEB Farbenfabrik Wolfen, Körnung 0.2–0.3 mm, beladen mit Wasserstoffionen, Austauschkapazität 33.6 mg K/cm und 28.6 mg Na/cm Harz), zum anderen Male in einer Anionenaustauschersäule (Durchmesser 120 mm, Höhe 550 mm, Austauscher: Wofatit L 150 der Fa. VEB Farbenfabrik Wolfen, Körnung 0.3–0.4 mm; zur Hälfte war die Säule mit EDTA und mit Oxalat beladen).

Aufschluss

Ca. 1 g Zinnwalditkonzentrat wurde mit einem Gemisch aus 5 ml conz. Salpetersäure und 10 ml Fluorwasserstoffsäure (40%-ig) dreimal aufgeschlossen und die zurückbleibende Substanz dreimal mit conz. Schwefelsäure abgeraucht. Anschliessend wurde mit 25 ml 50%-iger Schwefelsäure solange gekocht, bis die Lösung klar erschien (vgl. ELLESTAD UND HORSTMANN[1]).

TRENN- UND BESTIMMUNGSMETHODEN

(*a*) Zur direkten Flammenphotometrie wurde die aufgeschlossene Substanz auf 250 ml aufgefüllt und davon 25 ml zur Analyse verwendet. Es wurde gegen Rahmenlösungen, die die entsprechenden Mengen Natrium und Kalium enthielten, mit einem Li-Filter gemessen.

(*b*) Zur Auftrennung der Alkalien wurde eine Kationenaustauschersäule mit KPS 200 nach JENTZSCH UND FROTSCHER[2] eingesetzt. Es zeigte sich, dass infolge der anderen anwesenden Elemente wie Eisen, Aluminium, Mangan usw. die Säulen in Kürze blockiert wurden, sodass eine Abtrennung dieser Elemente vorher erfolgen musste.

(*c*) Die Abtrennung der Störelemente Eisen, Mangan, Aluminium, usw. wurde mit einem Anionenaustauscher Wofatit L 150 durchgeführt. Die Anordnung wurde bereits unter Apparatives geschildert (vgl. dazu SAMUELSON *et al.*[3-5]). Das Filtrat dieser Trennung wurde dann zwei bis dreimal mit 10 ml konz. Schwefelsäure abgeraucht, um die aus dem Austauscher eluierte organische Substanz zu zerstören. Wurde dies nicht getan, so wurde bei nachfolgender Kationentrennung der Kationenaustauscher unbrauchbar.

(*d*) Die Beseitigung der Störelemente Eisen, Aluminium usw. mit Cadmiumoxyd und basischem Bleicarbonat wurde nach ELLESTAD UND HORSTMANN[1] und nach SWEET, RIEMAN III UND BEUKENKAMP[6] durchgeführt, ehe die Alkalien mit Wofatit KPS 200 getrennt wurden.

Ergebnisse: Wie die Analysenwerte der Tabelle I von zwei Lithiumkonzentraten zeigen, tritt bei reiner Flammenphotometrie derartiger Erzkonzentrate ein erhöhter Li-Wert auf, und zwar bis 8% des Gesamtergebnisses, wenn die Li-Konzentrationen zwischen 2 und 4% Li_2O liegen.

TABELLE I

LITHIUM-GEHALTE DER UNTERSUCHTEN KONZENTRATE

Methode	*Li-Glimmer I* (% Li_2O)	*Li-Glimmer II* (% Li_2O)
a	3.40 ± 0.02	2.67 ± 0.02
c + a	3.22 ± 0.02	2.60 ± 0.02
c + b + a	3.14 ± 0.02	2.44 ± 0.02
d + a	3.36 ± 0.02	—

Die in der Rubrik "Methode" angegebenen Buchstaben sollen das Trenn- und Bestimmungsverfahren, wie bereits beschrieben, angeben. Die gefundenen Gehalte sind die wahrscheinlichsten Werte aus jeweils 50 Analysen. In Testgemischen, die die abzutrennenden Komponenten in gleichen Verhältnissen wie im Glimmer enthielten, wurde das Lithium nach jeder Operation 100%-ig innerhalb der Fehlergrenze wiedergefunden. Die Methode c + b + a ist die Genaueste.

ZUSAMMENFASSUNG

Die flammenphotometrische Bestimmung von Lithium in Zinnwalditkonzentraten wurde nach dem Abtrennen der Störelemente (Fe, Al, Mn, Ca, Mg, K, Na usw.) sowohl mittels Kationen- und Anionenaustauscher als auch mittels CdO oder basischen Bleicarbonates durchgeführt. Die reine Flammenphotometrie gab bis 8% zu hohe Lithiumwerte.

SUMMARY

The flame-photometric determination of lithium in Zinnwaldit-concentrates was carried out after removal of the interfering elements (Fe, Al, Mn, Ca, K, Na, etc.) either by means of cation and anion-exchange resins or by means of CdO or basic lead carbonate. Flame photometry alone resulted in up to 8% too high lithium values.

RÉSUMÉ

Une méthode photométrique de flamme est proposée pour le dosage du lithium dans des silicates. Les ions qui peuvent gêner le dosage sont éliminés soit par échangeurs d'ions, soit au moyen d'oxyde de cadmium ou de carbonate basique de plomb. La photométrie de flamme fournissait des valeurs du lithium jamais jusqu'à 8% trop élevées.

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THE REACTION OF SCHOENBERG'S REAGENT WITH ELEMENTAL SULFUR

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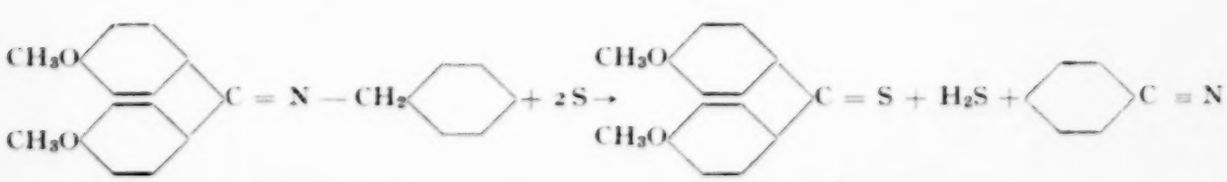
The reaction of elemental sulfur with various diphenyl-substituted compounds has been the object of rather extensive study in recent years, chiefly by MOREAU and co-workers[1]. They demonstrated that numerous compounds of this general type will react with sulfur at sufficiently high temperatures, yield H_2S and a corresponding thioketone, and, in certain cases, various other products.

The use of N-4,4′-(dimethoxybenzohydrilidene)benzylamine as a reagent for the detection of elemental sulfur was first proposed by SCHOENBERG AND URBAN[2] who observed that this compound could be reacted with elemental sulfur to yield 4,4′-dimethoxythiobenzophenone, H_2S and benzonitrile as recognizable products. The thioketone thus formed was of an intense blue color which was easily recognizable even in small quantities. Although they undertook no quantitative studies of the reaction, they reported the following over-all equation:



The first reported attempt to use the reaction for quantitative determination of sulfur was that of ORY, WARREN AND WILLIAMS[3] who showed that the reaction was quite suitable for colorimetric determinations. The relation between thioketone production and the quantity of sulfur present was not that which would be predicted

on the basis of the above equation for the reaction. Instead the thioketone produced corresponded to only about 0.25% of the sulfur present. The absolute quantity of thioketone produced was determined spectrophotometrically using the known optical density of the thioketone[4]. The discrepancy could not be explained on the basis of a deviation from the Beer curve since a plot of optical density *vs.* concentration of thioketone was found to be quite linear. An attempt was made by ORY *et al.*[3] to examine the mechanism of this reaction by a limited number of infrared spectral studies. While not conclusive, the study revealed that the reaction was complex and probably proceeded through one or more intermediates.

From the foregoing, it is seen that the practical application of SCHOENBERG's reagent for quantitative determination of elemental sulfur could be put on a more firm and less semi-empirical basis if an understanding of the mechanism of the reaction could be obtained. The most desirable approach to this problem seems to be that of infrared spectral analysis. Such an analysis of the reagent molecule would itself be of considerable intrinsic value since no extensive study of the benzohydrilidene structure has previously been reported.

The first requirement was to obtain, as completely as possible, an assignment of the infrared absorption spectrum of the reagent, $(CH_3OC_6H_5)_2C{=}NCH_2C_6H_5$. The results of this phase of the study are reported here. Their application to the investigation of the reaction mechanism is being studied further.

TABLE I

Compound	*Group(s) of interest*
Benzylamine	$-CH_2-N$
Benzalazine	$-C=N$
Benzylidene aniline	$-C=N$
Benzylidene benzylamine	$-C=N-CH_2$
Benzylidene methylamine	$-C=N-C$
Benzophenone	$-C(=O)-$
Benzophenone anil	$-C(-)=N$
4,4′-diaminobenzophenone	*p,p′*-disubstituted diphenyl
4,4′-dihydroxybenzophenone	*p,p′*-disubstituted diphenyl
4,4′-dimethoxybenzophenone	*p,p′*-dimethoxy diphenyl
4,4′-dimethylbenzophenone	*p,p′*-dimethyl diphenyl
diphenylmethane	$-C(-)-$
4,4′-dimethoxythiobenzophenone	$CH_3O-\ -C(=S)-\ -OCH_3$
p-methyl anisole	$C-\ -OCH_3$
p-methoxy anisole	$-O-CH_3$
Toluene	$-CH_3$

EXPERIMENTAL

Two sampling techniques were used in obtaining the spectrum of SCHOENBERG's reagent:

(*1*) pressed KBr disk technique;

(*2*) solution spectra using CS_2, CCl_4, and benzene as solvents.

Samples of the structurally similar solid compounds were prepared in the same manner. Liquid compounds were examined in thin cells or as films between rock salt plates.

All compounds used were obtained from Eastman Organic Chemicals Company with the exceptions of benzalazine, benzylidene-benzylamine and 4,4′-dimethoxythiobenzophenone which were prepared in these laboratories. The benzalazine was kindly supplied by Dr. HORACE ORY. The benzylidene-benzylamine was prepared by the method of MASON AND WINDER[5]. The 4,4′-dimethoxythiobenzophenone was prepared by the reaction of SCHOENBERG's reagent with elemental sulfur. The thioketone was distilled from the reaction mixture at a temperature of 205° and under pressure of 5 mm Hg.

All solids were purified by recrystallization from ethanol. All liquids were distilled under reduced pressure and the appropriate constant-boiling fraction was collected.

TABLE II

in cm^{-1}	*Assignment*	in cm^{-1}	*Assignment*
3030	aromatic CH	1117	CH_3
2941	nonaromatic CH	1050	C—N
2849	$-CH_2-$	1029	C—
1653	$-CH_2-R$, $R \neq H$		
1626 (sh)	C=N	995	mono substituted phenyl
1601	phenyl	943	—C—
		929	—C—
1513	*para* substituted phenyl	847	*para* substituted phenyl
1458	phenyl	833	*para* substituted phenyl
1418	CH_3	800	*para* substituted phenyl
1342	OCH_3		
1312	—C=	785	CH_3
1298	C—N	768	—C—
		749	—C—H
1250	OCH_3	736	mono substituted phenyl
1181	$-CH_2-$	697	mono substituted phenyl
1173	—C=	685	*para* substituted phenyl
1156	phenyl		

A Perkin-Elmer Model 21 Recording Infrared Spectrometer was used in obtaining all spectral data.

RESULTS AND DISCUSSION

Initial attempts to make definite assignments for all bands based purely on the generalized group frequency assignment given in the widely used chart by COLTHUP and in various standard references[6,7] met with little success. Accordingly, the spectra of a series of compounds having particular structural groupings in common with SCHOENBERG's reagent were examined. The compounds used together with the groups of interest in each are listed in Table I. The presence or absence of bands in the various spectra were then correlated to indicate the probable origin of band. The band frequencies of SCHOENBERG's reagent and their assignments are tabulated in Table II.

A definite suppression of the 847 cm^{-1} band (attributed to *para*-phenyl substitution) was observed in solution spectra of all compounds having this grouping. Spectra of pure liquids having this grouping showed no such suppression nor did there appear to be any in the solid-state spectra. The reason for this is not clearly understood although it presumably results from some type of solvent–solute interaction.

SUMMARY

The infrared absorption spectrum of SCHOENBERG's reagent, $(CH_3OC_6H_5)_2C=NCH_2C_6H_5$ has been obtained in the 650–5000 cm^{-1} region. Assignments have been made for all observed bands using group frequency methods.

RÉSUMÉ

Les auteurs ont étudié la réaction du réactif de SCHOENBERG avec le soufre. Le spectre d'absorption infra-rouge de ce réactif a été tracé entre 650 et 5,000 cm^{-1}.

ZUSAMMENFASSUNG

Beschreibung der IR-Spektren des SCHOENBERG'schen Reagenzes zur Bestimmung von Schwefel.

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ON THE USE OF BIS-CYCLOHEXANONE-OXALYLDIHYDRAZONE AND BIS-ACETALDEHYDE-OXALYLDIHYDRAZONE IN THE ANALYSIS OF COPPER

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INTRODUCTION

In the present publication bis-cyclohexanone-oxalyldihydrazone and bis-acetaldehyde-oxalyldihydrazone will be referred to as reagent 1 and reagent 2, respectively.

NILSSON[1] described the colour formation between copper(II) and the reagents 1 and 2. Other authors applied reagent 1 for the determination of copper in pulp and paper[2], plant materials[3], blood serum[4], steel[5-9], different metals and alloys[9-11] and in gelatine[12]. Some authors[13,14] introduced modifications in their methods of determining copper with reagent 1.

The use of reagent 2 in the analysis of copper is suggested in other papers[9,15], and a procedure has been published for the determination of copper in uranium[16].

The literature surveyed contained no data on the composition and stability of the complexes formed between copper and reagent 1 and 2. The statement by some authors that a considerable excess of reagent 1 was needed to maintain a constant extinction for some time indicated that the complex or the reagent were unstable in solution. An investigation was therefore started with the purpose of obtaining information on the applicability of the two reagents and on the complexes with copper.

INSTRUMENTS AND REAGENTS

Instruments

Extinction measurements were made with a Zeiss spectrophotometer PMQ II and 1.000-cm glass cells.

Current–voltage curves were recorded with a Sargent Polarograph Model XXI. The conventional type of dropping mercury electrode and a modified H-cell were used. Oxygen was eliminated before the electrolysis by passing pure nitrogen through the solutions for 10 min. A nitrogen atmosphere was kept over the solutions during electrolyses. An external saturated calomel electrode (SCE) served as reference electrode.

For potentiometric titrations and determinations of pH, a Beckman pH meter model H 2 and a Beckman Zeromatic pH meter were employed.

Reagents

The purity of reagent 1 (Hopkins and Williams Ltd.) was controlled by elementary

analysis and infrared absorption spectroscopy. No impurities were detected by these methods.

Reagent 2 was not applied in the solid state, but solutions of the copper(II)–reagent 2 complex were prepared by adding acetaldehyde to solutions of the copper (II)–reagent 1 complex. The higher stability of the former complex resulted in complete replacement of cyclohexanone by acetaldehyde.

The acetaldehyde was of purissimum quality. All other chemicals were of reagent grade quality. Copper-free distilled water was used.

EXPERIMENTAL

Standard solutions

A standard solution of copper(II) was prepared by dissolving 4.4 g of $CuSO_4 \cdot 5H_2O$ in 1000 ml of distilled water and determining the exact concentration by electrolysis. The standard solution was found to contain 1.12 mg of copper per ml corresponding to a molarity of $1.76 \cdot 10^{-2}$.

Reagent 1 is only slightly soluble in water and was therefore dissolved in 50% v/v ethanol. Due to the instability of the reagent only freshly prepared solutions were applied. (Reagent 1 is soluble in aqueous alkaline solutions, but in such solutions the reagent was found to be very unstable.)

Buffer solutions

Buffers consisting of primary and secondary phosphates (which do not form complexes with copper) and of ammonia and ammonium chloride were prepared. The pH of the phosphate buffer was 8.0 and of the two ammonia–ammonium chloride buffers 8.2 and 9.5 (determined by pH meter).

Ionic strength

All solutions prepared were 0.1 *M* with regard to potassium chloride.

Temperature

All experiments were carried out at 20° ± 1°.

Absorption curves

In the pH range 7–10 copper(II) ions react with reagent 1 and 2 forming a blue and a violet complex respectively. In Fig. 1 absorption curves of solutions of the two complexes and of the reagent blank are reproduced, all solutions being measured against distilled water.

It is seen from Fig. 1 that the absorption maximum of the copper(II)–reagent 2 complex varied with the buffer applied. With phosphate buffer (pH 8.0) the maximum was located at 510 mμ, while the use of the ammonia–ammonium chloride buffer (pH 9.5) resulted in a change of maximum to 545 mμ. This change of maximum may be due to the incorporation of ammonium ions in the copper(II)–reagent 2 complex. No similar effect of change of buffer was observed for the copper(II)–reagent 1 complex. (In earlier publications[13] it is stated that ammonium ions affected the colour formation between copper(II) and reagent 1.)

The absorption curves of the copper(II)–reagent 2 complex showed no signs of the presence of copper(II)–reagent 1 complex.

The different molar extinction coefficients in phosphate buffer pH 8.0 were found to be: $\varepsilon = 1.6 \cdot 10^4$ for the copper(II)–reagent 1 complex at 600 mμ; and $\varepsilon = 2.3 \cdot 10^4$ for the copper(II)–reagent 2 complex at 510 mμ.

For the copper(II)–reagent 2 complex (ammonia–ammonium chloride buffer pH 9.5) the molar extinction coefficient was found to vary considerably with the excess of reagent used, and therefore no value is given.

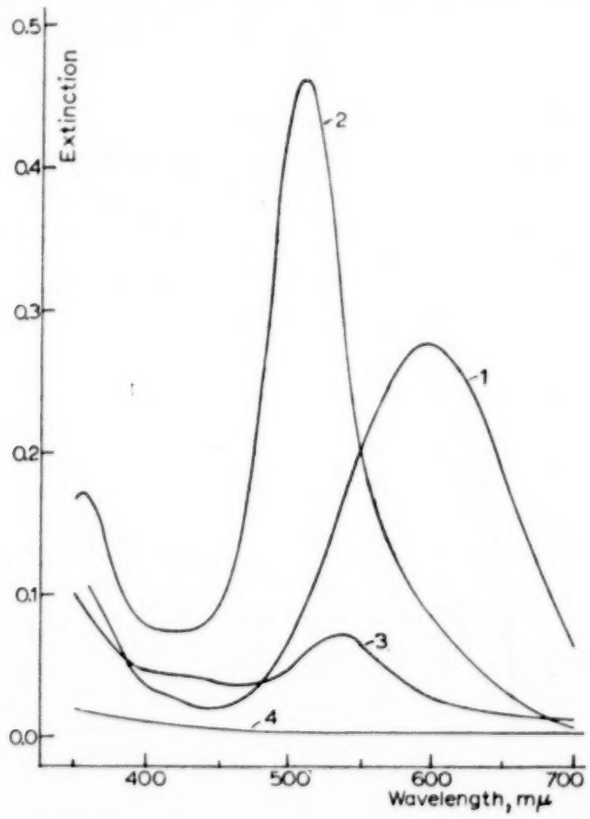


Fig. 1. Absorption curves of the copper(II) complexes with reagent 1 and 2. (1). Absorption curve of the copper(II)–reagent 1 complex, phosphate buffer pH 8.0; (2). Absorption curve of the copper-(II)–reagent 2 complex, phosphate buffer pH 8.0; (3). Absorption curve of the copper(II)–reagent 2 complex, ammonia–ammonium chloride buffer pH 8.2; (4). Absorption curve of a reagent 1 solution. All solutions were measured against distilled water.

INVESTIGATIONS OF REAGENT 1

With the normal four-coordination of copper(II) and presuming the ligand to be bidentate, a ligand–metal ratio of 2:1 was expected for the copper(II)–reagent 1 complex. Previous authors[4] have reported, however, that in the analysis of copper at least an eightfold excess of reagent 1 should be added in order to keep the extinction constant for some time. Our own preliminary photometric investigations with the purpose of elucidating the composition of the complex gave inconsistent results indicating the presence of 4–6 ligands. It was further observed that the blue colour of the complex developed slowly, and also that the colour disappeared again after a certain time. The colour faded and disappeared particularly rapidly in the presence of excess of copper.

Investigations by spectrophotometry

A fresh solution of reagent 1 containing phosphate buffer (pH 8.0) was prepared. From this solution aliquot parts were pipetted into 100-ml volumetric flasks after different times of standing. Copper(II) standard solution was added and the solutions were diluted to volume with distilled water. The concentration of reagent 1 and copper in the final solutions were $1.408 \cdot 10^{-4}\,M$ and $3.52 \cdot 10^{-5}\,M$, respectively. The extinctions of the solutions were measured at 600 mμ against distilled water after different times of standing at room temperature. From the series of measurements Fig. 2 was plotted.

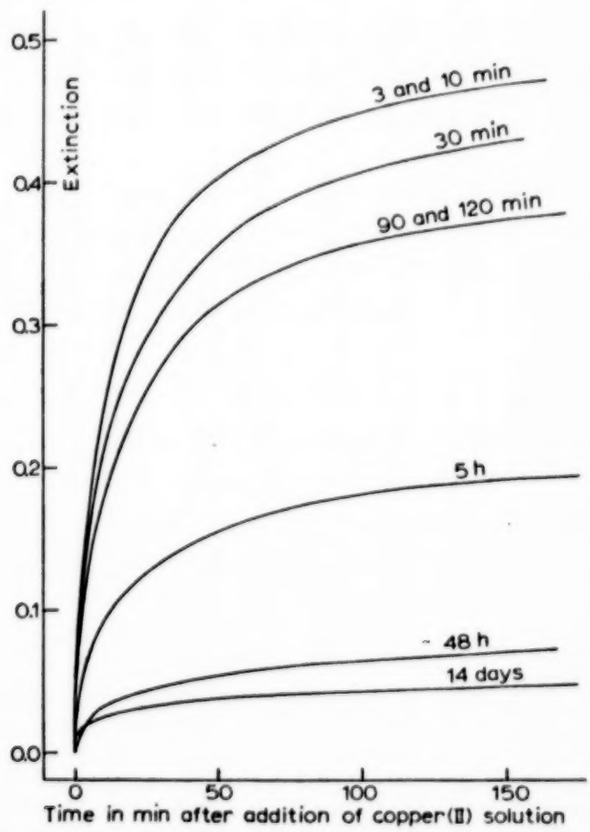


Fig. 2. Extinctions of a series of copper(II)–reagent 1 solutions measured after the addition of copper(II) solution to reagent 1 solutions which had been kept in phosphate buffer pH 8.0 for the time specified on the separate curves. All solutions contained $3.52 \cdot 10^{-5}\,M$ of copper and $1.408 \cdot 10^{-4}\,M$ of reagent 1. The extinctions were measured at 600 mμ against distilled water.

The experiment showed that the amount of reagent available for colour formation decreased on standing. In the experiment described above the ligand–metal ratio was 4:1. By diminishing the excess of ligand the rate of decomposition on standing increased, the highest rates being observed in the presence of ligand–metal ratios below 2:1.

The experiment also showed that the slow development of the blue colour was not due to complex formation between copper(II) ions and some decomposition product of reagent 1. In that case the extinctions measured after the addition of copper(II) ions would be expected to increase with the time of standing of the reagent 1 solution.

Investigations by polarography

Several polarograms of reagent I in ammonia–ammonium chloride and phosphate buffers were recorded. The polarograms exhibited only one irreversible wave with halfwave potential about —1.6 V *vs.* SCE. (A maximum on the curve was easily depressed by addition of a 0.005% solution of gelatine). It was not possible, however, to obtain a reproducible i_d/c value. The experiments showed that the diffusion current decreased with the time of standing of the reagent I solutions, indicating that the reagent decomposed in solution. No colour was obtained with copper(II) ions after the diffusion current had decreased to a minimum value. Some of the polarographic data are given in Table I.

TABLE I

DIFFUSION CURRENTS AND HALFWAVE POTENTIALS OF A $1.8 \cdot 10^{-3}$ *M* SOLUTION OF REAGENT I IN VARIOUS MEDIA

Buffer	*Time from mixing the solutions*	$E_{1/2}$ *(V vs. SCE)*	i_d *(μA)*
Phosphate, pH 8.0	17 h	—1.59	20.4
	15 d	—1.52	3.1
	37 d	—1.45	2.1
Ammonia–ammonium chloride, pH 8.2	3 d	—1.59	36.4
	15 d	—1.53	8.9
	37 d	—1.50	4.1
Ammonia–ammonium chloride, pH 9.5	1.5 h	—1.57	39.3
	3 d	—1.53	26.2
	7 d	—1.52	19.7
	37 d	—1.50	4.6

The rate of decomposition of the reagent was not reproducible. The decomposition was probably affected also by other factors than the time, *i.e.* pH, ionic strength, temperature, etc. The halfwave potential was found to shift to more positive values when the reagent decomposed. This shift was probably due to some decomposition product(s).

Current–voltage curves of the blue complex and excess of reagent I in ammonia–ammonium chloride and phosphate buffers exhibited two waves. The first wave ($E_{1/2}$ — 0.30 V *vs.* SCE) corresponded to a one-electron reduction of a copper(II) to a copper(I) complex, and the second wave ($E_{1/2}$ — 1.60 V *vs.* SCE) to reduction of the reagent in the complex and of excess of reagent. The plot of log $i/i_d - i$ *vs.* the applied potential for the copper wave showed a straight line with a slope of 0.06 V, indicating a reversible one-electron reduction. The reagent wave showed an irreversible reduction and the diffusion current decreased with the time.

Experiments in ammonia–ammonium chloride buffer containing the blue complex and only a slight excess of reagent I were also performed. Current–voltage curves were recorded at different time intervals after mixing the solutions. The diffusion current of the reagent wave decreased constantly and the wave of tetrammine–copper(II) ions appeared on the polarogram, showing that copper ions were liberated from the complex when the reagent decomposed.

Investigations by pH meter

A $3.27 \cdot 10^{-3}$ *M* solution of reagent 1 in 50% v/v of ethanol showed a pH of about 3. On titration with sodium hydroxide standard solution (0.1 *N*) the pH increased rapidly to about 8. The titration curve then rose less steeply to an inflection point at about pH 10, corresponding to an addition of 1 equivalent of base. Above pH 10 the curve flattened out.

In another experiment the pH of a $1.8 \cdot 10^{-3}$ *M* solution of reagent 1 dissolved in 50% v/v of ethanol was adjusted to 8.55 with sodium hydroxide solution. On standing the pH decreased and alkali was added to restore the original pH. On prolonged standing the additions of alkali needed decreased until after about a month the pH was nearly constant and the total amount of base added was nearly 1 equivalent.

In a third experiment a $1.44 \cdot 10^{-3}$ *M* solution of reagent in 50% v/v of ethanol was prepared and hydrochloric acid was added until pH 3.0. On standing, the pH was constant for a month, the only change observed being the appearance of a faint yellow colour.

Reagent 1 was easily soluble in aqueous sodium hydroxide solutions (pH 10), but the reagent decomposed rapidly and after a relatively short time the solutions did not produce the blue colour with copper(II) ions in the pH range 7–10.

In the pH range 7–10 the addition of copper(II) ions to a solution of reagent 1 resulted in a drop of pH indicating complex formation with liberation of hydrogen ions.

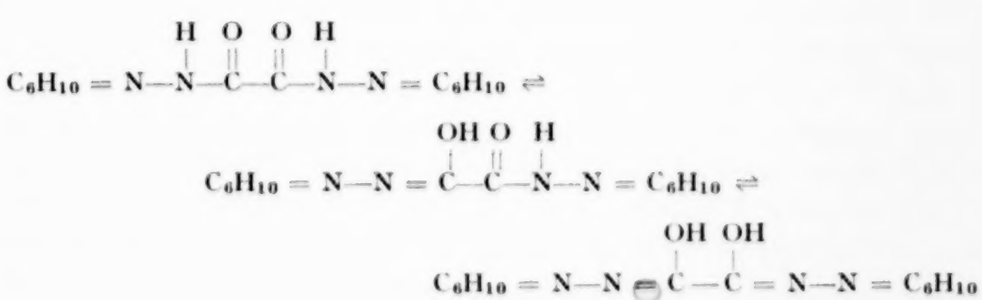
RESULTS AND DISCUSSION

Tautomerism of reagent 1

Infrared absorption spectra of reagent 1 in the solid state showed that the reagent occurred in the ketone form. In an acid solution of reagent 1 (pH about 3) the presence of the ketone form was indicated qualitatively by precipitation with 2,4-dinitrophenylhydrazine. In strongly alkaline, aqueous solutions (pH > 10) reagent 1 was believed to be present in the enolic form.

The blue complex between copper(II) and reagent 1 is stable in the pH range 7–10. In this intermediate pH range reagent 1 may be present in a partly enolized form.

The following equilibria are suggested for the tautomeric forms of reagent 1 in solution:

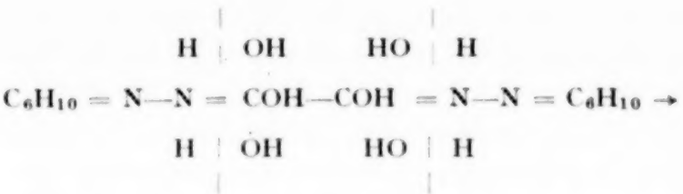


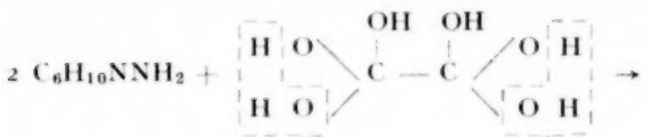
The slow development of the blue copper(II)–reagent 1 complex in the pH range 7–10 could be due to a slow enolization of the ketone form.

Decomposition of reagent 1

In alkaline aqueous solutions (pH > 10) reagent 1 decomposed rapidly. Among

the decomposition products oxalate ions and reducing agents were detected. The following irreversible decomposition scheme is proposed for reagent 1 in strongly alkaline solutions:





$$2\ C_6H_{10}NNH_2 + (COOH)_2 + 2\ H_2O$$

According to BALANDIN AND VASKEVICH[17] cyclohexanonehydrazone may react with water:

$$2\ C_6H_{10}NNH_2 + H_2O \rightarrow 2\ C_6H_{11}OH + N_2 + N_2H_4$$

to give cyclohexanol, nitrogen and hydrazine; or, in the presence of catalysts:

$$C_6H_{10}NNH_2 \rightarrow C_6H_{12} + N_2$$

to form cyclohexane and nitrogen. In the absence of catalysts and in the presence of cyclohexanone, cyclohexanonehydrazone may react as follows:

$$C_6H_{10}O + C_6H_{10}NNH_2 \rightarrow C_6H_{10}NNC_6H_{10} + H_2O$$

Some of these products, *e.g.* hydrazine, are reducing agents.

In the pH range 7–10 acid decomposition products were formed requiring one equivalent of base for neutralization. As in the strongly alkaline range reducing agents were detected, but not oxalate ions. On the basis of these observations the following reaction is suggested for the decomposition of reagent 1 in the pH range 7–10:

$$C_6H_{10}NNH_2 \rightarrow C_6H_{10}NNH_2 + C_6H_{10}{=}N{-}NH{-}CO{-}COOH + H_2O$$

The cyclohexanonehydrazone formed may react further as indicated above producing reducing agents.

In acid solution — pH about 3 — very little decomposition was found to take place. Neither reducing agents nor oxalate ions were detected. A yellow colour appeared, however, on standing, probably originating from a slight decomposition producing cyclohexanone.

The rate of decomposition of reagent 1 in the pH range 7–10 and above pH 10 was found to increase in the presence of copper(II) ions.

COMPLEX FORMATION OF COPPER WITH REAGENT 1

The decomposition of the copper(II)–reagent 1 complex in solution made it difficult to employ the standard spectrophotometric and polarographic methods for elucidating the composition and stability of the complex. With reagent 2, however, the complex formed with copper(II) was stable, and for this complex the ligand–metal ratio of 2:1 was found. Considering the structural similarity between the reagent 1 and the reagent 2 complexes it was deduced that a ligand–metal ratio of 2:1 was highly probable also for the blue complex. The following structure is therefore suggested for the complexes between copper(II) and the reagents 1 and 2.

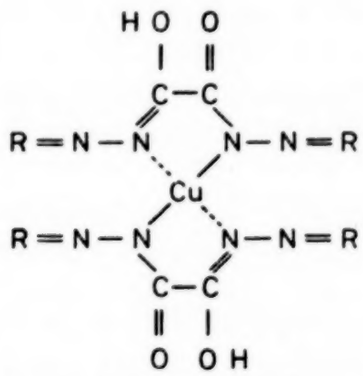


Fig. 3. Suggested structure in solution of the copper(II) complexes with reagent 1 and 2. The group marked R represents either CH_3CH or C_6H_{10}.

The decomposition of reagent 1 in the pH range 7–10 resulted in the formation of reducing agents which in turn may reduce the copper(II) ions. By polarography the presence of a colourless copper(I)–reagent 1 complex was indicated, but due to the instability of the system detailed investigations could not be carried out. As seen below a copper(I)–reagent 2 complex with 2 ligands was found polarographically, and this number of ligands is also probable for the similar copper(I)–reagent 1 complex.

Finally, complexes between copper and reagent 1 may exist in the acid and strongly alkaline range.

INVESTIGATIONS OF REAGENT 2 AND THE COPPER–REAGENT 2 COMPLEXES

Solutions of the complex between copper(II) and reagent 2 were prepared by mixing known volumes of solutions of copper(II) ions, reagent 1, phosphate buffer (pH 8.0) and excess of acetaldehyde. The colour of the blue complex appeared initially, but in the course of seconds the solution turned violet. The replacement of cyclohexanol by acetaldehyde was found to be complete as seen by the absorption curves of the complexes. The violet complex was found to be stable in the pH range 6–10.

The extinctions of solutions of the copper(II)–reagent 2 complex increased rapidly after preparation and reached a maximum after about 48 h at room temperature. The extinctions were then constant for months. In the presence of ammonium ions the extinctions decreased slowly on standing.

The stability of the violet complex in solution made possible a determination of the composition by the method of continuous variation, and a distinct maximum was obtained for the ligand–metal ratio 2:1. The molar ratio method confirmed this composition.

Qualitative experiments indicated that the violet complex had a stability constant intermediate between the copper(II)–ethylenediaminetetraacetate complex ($\log K = 16.2$ at pH 8.0) and the copper(II)–cyanide complex ($\log K = 25$). Attempts to calculate the stability constant from spectrophotometric data gave $\log K$-values which were apparently too low ($\log K$ about 10).

Current–voltage curves of the violet copper(II) complex exhibited three waves. The first wave corresponded to reduction of copper in the complex. The second and third wave were due to reduction of excess of acetaldehyde and of reagent 2, respectively. The irreversible reagent wave was partly overlapped by the acetaldehyde wave in solutions containing a large excess of the latter reagent.

In ammonia–ammonium chloride buffer the halfwave potential of the copper wave in the complex was —0.30 V *vs.* SCE. Tetrammine-copper(II) ions in the same medium are reduced at a more positive potential. Consequently, it was possible to determine excess of copper in the presence of copper(II) complex. Polarograms of several solutions containing copper and different amounts of reagent 2 were recorded, and the diffusion current of tetrammine-copper(II) ions was plotted against the ligand–metal ratio of the solutions. The diffusion current of copper(II) decreased linearly with increasing amounts of reagent 2 and became equal to the residual current at the ligand–metal ratio 2:1 in accordance with the result obtained by spectrophotometry.

Several polarograms of the complex in ammonia–ammonium chloride and phosphate buffers and with a varying excess of reagent 2 were recorded. In all solutions the plot of $\log i/i_d - i$ *vs.* the potential of the copper wave showed a straight line with the slope 0.06 indicating a reversible one-electron reduction to a copper(I) complex. The halfwave potential was constant independent of the supporting electrolyte and of excess of reagent 2 showing a ligand–metal ratio of 2:1 also for the copper(I) complex. This complex is probably colourless, as it was not detected with the spectrophotometer.

The possible structure of the copper(II)–reagent 2 complex is shown in Fig. 3 (*vide supra*).

The violet complex between copper(II) and reagent 2 has been found to be much more stable in the solutions examined than the corresponding blue complex, and it has a higher molar extinction coefficient, is easily prepared and is therefore to be recommended for spectrophotometric determination of copper.

ACKNOWLEDGEMENT

The authors are indebted to PROF. HAAKON HARALDSEN for his interest in this investigation and for the facilities placed at their disposal.

SUMMARY

The reagents bis-cyclohexanone-oxalyldihydrazone (reagent 1) and bis-acetaldehyde-oxalyldihydrazone (reagent 2) and their complexes with copper were examined by spectrophotometry and polarography. The investigations indicated that in solution reagent 1 existed in three tautomeric

forms depending of the pH of the solvent. The decomposition of these forms was studied and decomposition schemes are suggested. In the pH range employed for spectrophotometric determination of copper (7–10), solutions of reagent 1 and the copper(II)–reagent 1 complex were found to be very unstable owing to the decomposition of the ligand. Solutions of reagent 2 and its complexes with copper were found to be much more stable. The investigations further indicated that both reagents form copper(II) complexes with ligand–metal ratios 2:1. In addition a colourless copper(I)–reagent 2 complex with two ligands was found polarographically. The existence of a similar complex between copper(I) and reagent 1 is probable.

RÉSUMÉ

Les auteurs ont effectué une étude spectrophotométrique et polarographique des complexes du cuivre, obtenus avec les deux réactifs suivants: bis-cyclohexanone-oxalyldihydrazone (réactif 1) et bis-acétaldéhyde-oxalyldihydrazone (réactif 2). Le réactif 1 peut exister sous trois formes tautomères, suivant le pH; les solutions du réactif 2 et de ses complexes avec le cuivre sont plus stables que celles du réactif 1.

ZUSAMMENFASSUNG

Untersuchung über die Verwendung von Bis-cyclohexanon-oxalyl-dihydrazon (Reagenz 1) und Bis-acetaldehyd-oxalyl-dihydrazon (Reagenz 2) zur spectrophotometrischen und polarographischen Bestimmung von Kupfer. Reagenz 1 existiert in 3 tautomeren Formen in Abhängigkeit von pH und Lösungsmittel. Es fölgen Angaben über die Zusammensetzung der Komplexe und deren Stabilität.

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Short Communications

Determinations of stability constants

The following method allows the determination of stability constants for complexes containing no more than two ligands, without the need to resort to graphical procedures. In the particular case chosen, the concentration of the ion under investigation was determined potentiometrically.

Solutions are said to be "corresponding" when they differ in C_M (total concentration of metal) and C_L (total concentration of ligand) but have the same average ligand number, $\bar{n}$. It has been shown[1], that if for two solutions the ratio metal : ligand is changed until the potential difference (E_M) due to the formation of complex is the same for both, the solutions are "corresponding".

$$E_M = E_0 - E$$

$$= \left(E_k + \frac{RT}{nF} \ln C_M\right) - \left(E_k + \frac{RT}{nF} \ln [\mathrm{M}]\right)$$

$$= \frac{RT}{nF} \ln \frac{C_M}{[\mathrm{M}]}$$

E_0 = e.m.f. of cell when no ligand has been added
E = e.m.f. of cell after addition of ligand
E_k includes the potential of the reference electrode, liquid junction potential, and activity coefficients.

$C_M/[\mathrm{M}]$ can thus be determined for when the solutions are "corresponding". For corresponding solutions

$$\bar{n} = \frac{C_L' - C_L}{C_M' - C_M}$$

and thus $\bar{n}$ can be determined. For a complex containing only two ligands

$$\bar{n} = 2 - \frac{[\mathrm{ML}]}{C_M} - \frac{2[\mathrm{M}]}{C_M}$$

$[\mathrm{M}]/C_M$ and $\bar{n}$ are both known so that [ML] can be calculated. All the information required to calculate the stability constants β_1 and β_2 is now available.

The above method was applied to the silver–pyridine system, the silver ion concentration being determined by means of a silver–silver bromide electrode, the reference electrode being a calomel electrode. The following values were obtained at 25°, the ionic strength of the solution being maintained at 0.1 by addition of the requisite amount of potassium nitrate:

$$\log \beta_1 = 1.90$$

$$\log \beta_2 = 4.25$$

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Elimination of aluminium interference in colorimetric determination of fluoride in water

Aluminium and fluoride when present together in natural water form a complex of great stability which interferes in the colorimetric determination of fluoride by the zirconium–alizarin method. For this determination MEGREGIAN[1] used correction curves, implying the previous determination of aluminium. To avoid that determination and eliminate the aluminium interference we have developed a separation by solvent extraction.

Precipitation of aluminium 8-hydroxyquinolate in presence of ammonium ions has been reported to separate aluminium from phosphorus, arsenic, fluorine and boron[2]. According to GENTRY AND SHERRINGTON[3] a 1% solution of 8-hydroxyquinoline in chloroform gives complete extraction of aluminium from an aqueous layer. The chloroform layer can be separated and its absorbance measured for aluminium. Studying the pH effect the same authors found that extraction is complete in two pH ranges: from 4.5–6.5 and from 8–11.5.

It thus seemed possible to use 8-hydroxyquinoline in chloroform to separate aluminium from fluoride, both in trace concentrations. Natural water is first buffered at pH 10 and then extracted, the aqueous layer being analysed for fluoride. The fluoride contents of many natural water samples showed good agreement with previous results and no effect of aluminium interference.

Procedure

Place in a 250-ml separatory funnel 25 ml of water with 1.2038 g of powdered ammonium chloride and 22.5 ml of 1 *M* ammonium hydroxide to buffer the solution at pH 10. Dilute the volume to 50 ml with distilled water. Add 10 ml of a 1% solution of 8-hydroxyquinoline in chloroform and shake the funnel steadily for 6 min. Allow the layers to settle, and run off the organic layer. Then remove the aqueous layer to a 100-ml stoppered flask, and adjust its pH to 5–7 with 1 : 1 hydrochloric acid. Fluoride is then colorimetrically determined by the zirconium–alizarin method.

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Book Review

The Analysis of Titanium and its Alloys, 3rd ed., Imperial Chemical Industries Ltd., London, 1959, 119 pp., price 21 s.

The appearance of a third edition of this book in less than three years indicates the importance of the subject under consideration and also of the usefulness and quality of this work.

As in the previous editions, one or more reliable analytical procedures are described in detail for each of more than twenty-five elements which can be present in titanium alloys. Also included are sampling procedures for the various forms of titanium metal and a semi-quantitative spectrographic identification method. An additional chapter is devoted to the identification of titanium alloys by means of simple, non-destructive spot tests on the metal surface.

Some of the earlier procedures have been modified or replaced by quicker or more convenient methods. An entirely new amperometric method for the determination of chlorine replaces the turbidimetric method. A procedure for determining boron, a more sensitive method for the analysis of nitrogen, an additional procedure for determining carbon, a differential absorptiometric procedure for the determination of large amounts of molybdenum and some others appear for the first time.

This third edition is strongly recommended to all chemists with analytical problems involving titanium and its alloys.

F. VERBEEK (Ghent)

Anal. Chim. Acta, 24 (1961) 591

Announcements

THE GORDON RESEARCH CONFERENCES

12 June–1 September 1961

The Gordon Research Conferences for 1961 will be held from 12 June to 1 September at Colby Junior College, New London, New Hampshire; New Hampton School, New Hampton, New Hampshire; Kimball Union Academy, Meriden, New Hampshire; and Tilton School, Tilton, New Hampshire.

Purpose. The conferences were established to stimulate research in universities, research foundations and industrial laboratories. This purpose is achieved by an informal type of meeting consisting of scheduled lectures and discussion groups.

It is hoped that each conference will extend the frontiers of science by fostering a free and informal exchange of ideas among persons actively interested in the subjects under discussion. The purpose of the program is to bring experts up to date on the latest developments, to analyze the significance of these developments and to provoke suggestions concerning the underlying theories and profitable methods of approach for making progress. The review of known information is not desired.

Registration and reservations. Attendance at the Conferences is by application. Individuals interested are requested to send their applications to the Director at

least two months prior to the date of the Conference. *All applications must be submitted in duplicate on the standard application form which may be obtained by writing to the office of the Director.* This procedure is important because certain specific information is required in order that a fair and equitable decision on the application may be made. Attendance at each Conference is limited to approximately 100 conferees.

The Board of Trustees of the Conferences has established a fixed fee of $100 for resident conferees at each Conference. The fixed fee will cover registration, room (except room with private bath or single room), meals and gratuities. Conferees living at the Conference location who will pay all or part of the fixed fee as a personal expense may request a reduction of $25 in the fixed fee. Application for this special fee ($75) must be made when the registration card is returned to the Director.

Limited accommodation is available for wives and families.

Attendance. Requests for attendance at the conferences, or for additional information, should be addressed to W. GEORGE PARKS, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. From 12 June to September 1961 mail for the office of the Director should be addressed to Colby Junior College, New London, New Hampshire.

The program of the *Analytical Chemistry Conference* which will be held on 14–18 August 1961 at New Hampton School, New Hampton, N.H., with SIDNEY SIGGIA as Chairman, and DONALD D. DEFORD as Vice-Chairman, is as follows:

14 Aug.
C. B. MURPHY, Differential Thermal Analysis.
D. J. FRAADE, Continuous Analysis.

15 Aug.
I. FANKUCHEN, The Application of X-Rays to Structure Determination of Organic Materials.
L. S. BIRKS, The Electron Probe.

16 Aug.
H. FISCHBACH, J. W. COOK, L. L. RAMSEY, Analysis and Food and Drug Regulations.
W. W. BATES, Analysis and Composition of Tobacco Smoke.

17 Aug.
J. E. LOVELOCK, Electron Affinity Spectroscopy.
Open Session.

18 Aug.
G. A. HARLOW, New Developments in the Determination of Acids and Bases.

Other conferences will be held on Petroleum, Catalysis, Polymers, Textiles, Elastomers, Corrosion, Medicinal Chemistry, Separation and Purification, Instrumentation, Food and Nutrition, Cancer, Chemistry of Coal, Chemistry and Physics of Liquids, Proteins, Scientific Information Problems, Magnetic Resonance, Radiation Chemistry, Organic Reactions, Steroids and other Natural Products, Statistics in Chemistry and Chemical Engineering, Inorganic Chemistry, Adhesion, Lipid Metabolism, Cell Structure and Metabolism, Physical Metallurgy, Vitamins and Metabolism, Chemistry etc. of Bones and Teeth, Organic Coatings, Chemistry at Interfaces, Solid State Studies in Ceramics, Toxicology and Safety, Chemistry and Physics of Solids, Photonuclear Reactions, High Temperature Chemistry, Ion Exchange, Chemistry and Metallurgy of Semiconductors, Microbiological Deterioration, Biochemistry and Agriculture, Electrodeposition, Glass.

JOINT CONFERENCES
NUCLEAR REACTOR CHEMISTRY
ANALYTICAL CHEMISTRY IN NUCLEAR REACTOR TECHNOLOGY

The Second Conference on Nuclear Reactor Chemistry and the Fifth Conference on Analytical Chemistry in Nuclear Reactor Technology will be held at Gatlinburg, Tenn. (U.S.A.), on October 10, 11 and 12, 1961, under the sponsorship of Oak Ridge National Laboratory which is operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.

Second Conference on Nuclear Reactor Chemistry. The chemical behavior of reactor materials will be emphasized at this conference. Subjects for discussion include: chemical behavior of moderator and coolant materials and the effects of nuclear radiation on their properties; deportment of fission products in reactor fuels; development of reactor fuel and blanket materials; the application of statistical methods and computer calculations in planning and evaluation of experiments. Papers on these and other topics of interest to reactor chemists will be welcomed.

Fifth Conference on Analytical Chemistry in Nuclear Reactor Technology. This conference will be devoted to improved methods and instruments for the analysis of many nuclear materials and products. Papers are especially solicited on the following or related subjects: measurements of burn-up of uranium or plutonium fuels; isotopic analysis; determination of gases in reactor materials; methods and instruments for on-line analyses; remote analysis of radioactive materials; non-destructive testing of nuclear fuel elements and other reactor materials; analysis of (*a*) Be, BeO, cermets containing BeO, (*b*) Zr and Nb alloys, (*c*) heavy water, (*d*) plutonium and plutonium-base fuels.

In addition to papers setting forth specific achievements, review papers critically evaluating the *state of the art* with respect to any of the foregoing subjects are solicited.

Authors are requested to submit an abstract of 200 to 400 words of their paper, not later than July 15, 1961, and, at the same time, to indicate the time required for the presentation, not to exceed 20 minutes.

Proceedings of these conferences are to be published. Manuscripts of papers for publication should be submitted prior to or at the time of the conferences.

Abstracts of papers and inquiries regarding these conferences should be directed to the Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tenn. (U.S.A.), Attention:

W. R. GRIMES for Nuclear Reactor Chemistry

and

C. D. SUSANO for Analytical Chemistry

Inquiries concerning lodging or requests for reservations should be directed to: Reservation Services, Chamber of Commerce, Gatlinburg, Tenn. (U.S.A.).

SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 24, No. 1, January 1961

PHYSICAL PROCEDURES FOR THE ANALYSIS OF MIXTURES OF POLYCHLOROETHANES

A mixture of seven polychloroethanes has been analysed by fractionation into binary mixtures using a combination of continuous fractionation and the technique of total reflux with intermittent take-off. The binary mixtures were analysed by refractive index measurements. The relationship between binary mixture refractive index and component mass fraction was found to be linear. The temperature dependence of the refractive indices of the polychloroethanes over the range, 15–35°, was also determined.

J. S. RATCLIFFE, *Anal. Chim. Acta*, 24 (1961) 2–4

A RAPID METHOD FOR THE DETERMINATION OF AMMONIA (COMBINED) AND PHOSPHATE IN THE SYSTEM OF DIAMMONIUM PHOSPHATE AND DIPOTASSIUM PHOSPHATE

In systems containing $(NH_4)_2HPO_4$ and K_2HPO_4, it is possible to determine ammonium and phosphate ions by titrating 2 aliquots using methyl orange as the only indicator. Potassium can be calculated by difference. About 20 min are required for a single analysis.

B. PASCHKES AND B. BERNAS, *Anal. Chim. Acta*, 24 (1961) 5–10

DETERMINATION OF VERY SMALL QUANTITIES OF CARBON DIOXIDE AND ANALYTICAL APPLICATION OF THE METHOD

(in German)

A volumetric method for the determination of very small quantities carbon dioxide is described. The procedure gives very satisfactory results and can be applied for the determination of carbon in organic compounds.

E. SCHULEK, J. TROMPLER, A. ENDRÖI-HAVAS AND I. REMPORT, *Anal. Chim. Acta*, 24 (1961) 11–19

THE ACCURATE DETERMINATION OF COBALT

II. GRAVIMETRIC METHODS AND IN PARTICULAR THE PHOSPHATE METHOD

Some gravimetric methods for determining cobalt have been examined in order to assess their value for the accurate determination of the metal. The electrolytic method was found to give high results (about 1.4%), and the anthranilate method slightly high results (0.2 – 0.3%). A modification of the phosphate method has been developed in which a former drawback, the solubility of $CoNH_4PO_4 \cdot H_2O$, has been overcome using a rapid spectrophotometric determination of residual cobalt. The final procedure developed has been found to give accurate results (±0.1 – 0.2) and its use is recommended where this degree of accuracy is required.

A. G. FOSTER AND W. J. WILLIAMS, *Anal. Chim. Acta*, 24 (1961) 20–32

GRAVIMETRIC DETERMINATION OF MOLYBDENUM AND ITS SEPARATION FROM OTHER METALS WITH N-BENZOYLPHENYLHYDROXYLAMINE

N-Benzoylphenylydroxylamine is employed as a precipitant for the determination of molybdenum(VI). The precipitate can be weighed either directly or as molybdenum trioxide after ignition. Molybdenum can be determined in the presence of appreciable amounts of iron(III), cobalt(II), copper(II), chromium(VI) and vanadium(V).

S. K. Sinha and S. C. Shome, *Anal. Chim. Acta*, 24 (1961) 33–36

GRAVIMETRIC DETERMINATION OF BERYLLIUM WITH N-BENZOYLPHENYLHYDROXYLAMINE

N-Benzoylphenylhydroxylamine has been employed in the gravimetric determination of beryllium and in its separation from iron, aluminium and titanium. After suitable adjustment of pH iron, aluminium or titanium is precipitated quantitatively with the reagent; beryllium is subsequently precipitated after raising the pH of the filtrate. The metal may be determined by either igniting the precipitate to beryllium oxide or weighing it as $Be(C_{13}H_{10}O_2N)_2$.

J. Das and S. C. Shome, *Anal. Chim. Acta*, 24 (1961) 37–40

IMPURITY DETERMINATION BY THERMAL ANALYSIS

II. THE MELTING CURVE OF A QUICKLY FROZEN SAMPLE

A temperature-heat content relation is derived for a homogeneous solid solution of a binary system showing a very restricted rate of diffusion in the solid. It is shown experimentally that quickly frozen samples behave like homogeneous solid solutions. According to the new theory the depressions determined on partly molten samples are usually small and depend on the conditions; thus purity determinations based on heating curves of quickly frozen samples are of dubious value. The theory shows that superheating of the solid may occur when a solid solution is melted; this is confirmed experimentally.

H. F. van Wijk and W. M. Smit, *Anal. Chim. Acta*, 24 (1961) 41–45

THE ASSAY OF SODIUM CITRATE AND SODIUM POTASSIUM TARTRATE BY CATION EXCHANGE AND NON-AQUEOUS TITRIMETRY

Sodium citrate and sodium potassium tartrate are assayed by passing aqueous solutions of the salts through cation exchange resin columns, concentrating the effluents from the columns, and then titrating the effluents with standard sodium hydroxide solution. Sodium citrate is assayed by titrating a solution of the salt in glacial acetic acid with standard acetous perchloric acid, the end-point being detected potentiometrically; sodium potassium tartrate is assayed by stirring the salt in excess standard acetous perchloric acid, and then back-titrating the excess acetous perchloric acid with standard acetous potassium acetate, the end-point being detected potentiometrically.

M. L. Richardson, *Anal. Chim. Acta*, 24 (1961) 46–54

MICRODETERMINATION OF COBALT IN REACTOR-GRADE ZIRCONIUM
(in French)

A method is described for the separation and determination of cobalt in 100 mg reactor-grade zirconium. Separation is effected by means of an ion-exchange resin. After elution, the cobalt is purified by extraction with dithizone and determined spectrophotometrically with the help of nitroso-R-salt. With this method a content of 0.0003% can be determined with an accuracy of ±4%.

J. VOGEL, D. MONNIER AND W. HAERDI, *Anal. Chim. Acta*, 24 (1961) 55–60

DETERMINATION OF HIGHER MOLECULAR WEIGHT ALIPHATIC ALDEHYDES AND KETONES

The visible absorption spectra have been measured for the reaction products formed by aldehydes and ketones with *p*-nitrobenzenediazonium fluoborate in a phosphoric acid-2-methoxyethanol solvent medium. The absorption maxima for the reaction products of higher molecular weight aldehydes and ketones are much more intense than those formed by formaldehyde, acetaldehyde and acetone. This intensity effect has been used to analyze for propionaldehyde in mixtures also containing formaldehyde, acetaldehyde or acetone. The nature of the reaction products are considered.

A. P. ALTSHULLER AND I. R. COHEN, *Anal. Chim. Acta*, 24 (1961) 61–66

A METHOD FOR THE DETERMINATION OF STARCH IN WOOD

A rapid and simple method of estimating starch in wood is described which is suitable for carrying out large numbers of determinations.

F. R. HUMPHREYS AND J. KELLY, *Anal. Chim. Acta*, 24 (1961) 66–70

THE DETERMINATION OF LEAD IN COPPER-BASE ALLOYS AND STEEL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

The principle of atomic absorption spectrophotometry has only recently been exploited as an analytical technique and details are given of the development of a procedure for determining lead in copper-base alloys and leaded steels. The recommended method is simple, rapid and provides results as accurate as those obtained by the more time-consuming alternative methods in current use.

W. T. ELWELL AND J. A. F. GIDLEY, *Anal. Chim. Acta*, 24 (1961) 71–78

CONDUCTOMETRIC TITRATION OF METAL ACETATES IN AQUEOUS MEDIUM

Fifteen metal acetates in aqueous medium have been conductometrically titrated with trichloroacetic acid. The method has been applied to the titration of mono- and bivalent metals and angles at the equivalence point are sharp enough to allow accurate results to be obtained. Metal salts of acids weaker than acetic can be determined following solution in an excess of acetic acid and titration, because the weaker acid which is displaced does not interfere.

F. GASLINI AND L. Z. NAHUM, *Anal. Chim. Acta*, 24 (1961) 79–82

AMPEROMETRIC ARGENTIMETRIC AND MERCURIMETRIC TITRATION OF SULFHYDRYL

I. ARGENTIMETRIC TITRATION

Results of amperometric argentimetric titrations at the rotated platinum wire electrode in ammonia buffers of cysteine, glutathione, thioglycolic acid and 2-mercaptoethanol are presented. The method gives satisfactory results with glutathione and 2-mercaptoethanol. Thioglycolic acid gives good results in the presence of sulfite but high results in its absence. Its disulfide can be titrated accurately in the presence of sulfite. In agreement with other workers it was found that cysteine yields high results. The error increases with increasing cysteine concentration and is reduced in the presence of 0.1 *M* sulfite. It becomes equal to zero at cysteine concentrations equal to or smaller than $5 \cdot 10^{-5}$ *M*.

I. M. KOLTHOFF AND J. EISENSTÄDTER, *Anal. Chim. Acta*, 24 (1961) 83–90

PRECISION NULL-POINT POTENTIOMETRY

DIRECT MICRODETERMINATION OF IODIDE IN SOLUTIONS WITH HIGH CHLORIDE CONCENTRATIONS

The determination of microamounts of iodide in the presence of large concentrations of chloride, such as found in brines or iodized salt, can be performed directly and rapidly by the precision null-point potentiometric method. The complete analysis time is about 3 min. Iodized salt samples containing 5–100 p.p.m. iodide were determined with an average deviation less than 0.3 p.p.m. and with relative errors of about 0.5% at 100 p.p.m. and about 5% at 10 p.p.m. iodide. The measured samples contained 1–20 μg of iodide in 20 ml of solution, and the sodium chloride to iodide weight ratio was as high as 200,000 to 1. Similar precision and accuracy were obtained for prepared brines containing 10–200 p.p.m. iodide and a wide range of chloride to iodide ratios.

H. V. MALMSTADT AND J. D. WINEFORDNER, *Anal. Chim. Acta*, 24 (1961) 91–96

COLORIMETRIC DETERMINATION OF STRONTIUM

(Short Communication; in German)

R. PALOUŠ AND S. MIZERA, *Anal. Chim. Acta*, 24 (1961) 96–97

SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 24, No. 2, February 1961

THE EFFECT OF VARIATIONS IN BAROMETRIC PRESSURE AND OTHER FACTORS ON THE EBULLIOSCOPIC DETERMINATION OF MOLECULAR WEIGHTS, WITH SPECIAL REFERENCE TO THE USE OF THE MENZIES DIFFERENTIAL THERMOMETER

A theoretical treatment of the effect of variations in barometric pressure and other factors on the ebullioscopic determination of molecular weights leads to general expressions relating the variations in barometric pressure with the ebullioscopic constant of the solvent and with the temperature sensitivity of the MENZIES differential thermometer. Since these variations can affect significantly the accuracy of ebullioscopic molecular weight determinations, a single comprehensive correction term is calculated for each of the usual combinations of ebullioscopic solvent and thermometer filling liquid; this term enables results obtained at different pressures to be corrected to standard atmospheric pressure, thus eliminating the pressure effect. Finally a statistical analysis of some experimental results illustrates the validity of the correction term for the combination of benzene as ebullioscopic solvent with benzene as thermometer filling liquid.

S. KAMINSKY, *Anal. Chim. Acta*, 24 (1961) 101–112

APPLICATION OF THE DOUBLE WITHDRAWAL COUNTERCURRENT EXTRACTION TECHNIQUE TO ANALYTICAL CHEMISTRY

Application of the double withdrawal countercurrent extraction technique to chemical analysis has been singularly neglected, probably because of the complexity and tediousness of the associated mathematics. Present day computer technology proved to be readily applicable to the problem and information is presented which indicates the possible importance of this separation method to chemical analysis.

J. O. HIBBITS, *Anal. Chim. Acta*, 24 (1961) 113–120

TITRIMETRIC METHODS FOR THE MICRODETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS BY THE RAPID COMBUSTION PROCEDURE

I. THE DETERMINATION OF INDIVIDUAL HALOGENS

A critical study has been carried out of titrimetric methods suitable for the microdetermination of each of the halogens, chlorine, bromine and iodine, in their possible organic combinations with the elements, oxygen, nitrogen and sulphur, following organic decomposition by the rapid empty tube combustion procedure.

J. E. FILDES AND A. M. G. MACDONALD, *Anal. Chim. Acta*, 24 (1961) 121–127

KINETICS OF DECOMPOSITION OF YTTRIUM, CEROUS AND ZIRCONYL OXALATES

The kinetics of the decomposition of yttrium, cerous and zirconyl oxalates have been studied thermogravimetrically and also by differential thermal analysis.

R. P. AGARWALA AND M. C. NAIK, *Anal. Chim. Acta*, 24 (1961) 128–133

ANION EXCHANGE STUDIES OF ZIRCONIUM(IV) IN CITRATE SOLUTION

SEPARATION FROM MIXTURES

The anion exchange behaviour of zirconium(IV) in a citrate system is described. Nitric acid, hydrochloric acid, perchloric acid and ammonium chloride were tested as eluants on Dowex 21 K column. Zirconium is separated from fission product elements *e.g.*, barium, strontium, cadmium, caesium, molybdate and also from lead.

S. M. KHOPKAR AND A. K. DE, *Anal. Chim. Acta*, 24 (1961) 134–137

ION EXCHANGE RESINS IN STEEL ANALYSIS

The metals vanadium, chromium and molybdenum may be separated from the other constituents of steel by passing an acetate buffered solution of the steel through a strongly basic anion exchanger and selectively eluting the above metals from the resin column with aqueous solutions of 0.6 *N* sodium hydroxide, 8 *N* hydrochloric acid and 1 *N* hydrochloric acid, respectively.

F. M. HALL AND A. BRYSON, *Anal. Chim. Acta*, 24 (1961) 138–142

USE OF CARBOXYLIC ACID CATION EXCHANGE RESIN IN THE ANALYSIS OF COPPER IN CHROMATED WOOD PRESERVATIVE SOLUTIONS

An ion exchange separation, using carboxylic acid resin, combined with a thiosulphate titration is suggested as a rapid and accurate method for the determination of copper in chromated wood preservatives.

R. A. EDGE, *Anal. Chim. Acta*, 24 (1961) 143–145

THE APPLICATION OF CHELATE SYSTEMS TO PARTITION CHROMATOGRAPHY: PRELIMINARY PAPER

It has been found possible to retain solutions of chelating agents on a solid supporting medium, and in this paper preliminary investigations are reported which were carried out to determine the extraction behaviour of radioactive copper between an aqueous hydrochloric acid phase and a solution of dithizone in an organic solvent retained on silica gel. Chloroform was found to be a very satisfactory solvent and carbon tetrachloride was also used. For both of these solvents the extraction *vs.* acidity curves were found to be similar to the corresponding liquid–liquid extraction The high values for the fraction extracted show that this method would provide a useful technique for the concentration of copper from aqueous solution, and the similarity between the liquid–liquid and liquid–solid extractions suggests that it may be possible to adapt conventional liquid–liquid extractions to work on the column principle.

T. B. PIERCE, *Anal. Chim. Acta*, 24 (1961) 146–152

COLORIMETRIC DETERMINATION OF URANIUM(VI)

A new, very sensitive reagent is proposed for the colorimetric determination of uranium(VI), namely 1-phenyl-3-methyl-4-(3′-carboxy-4′-hydroxyphenyl-azo)-pyrazol-5-one.

GH. BAIULESCU AND I. C. CIUREA, *Anal. Chim. Acta*, 24 (1961) 152–154

UTILISATION OF PHENYLARSONIC ACID IN TURBIDIMETRY

DETERMINATION OF TANTALUM

(in French)

A turbidimetric method is described for the determination of tantalum with phenylarsonic acid. The method is fast and rarely requires preliminary separation. The only interfering elements are zirconium and niobium when present in molar ratios greater than Nb : Ta = 1 and Zr : Ta = 5.

R. SAINT-JAMES ET T. LECOMTE, *Anal. Chim. Acta*, 24 (1961) 155–160

THE RAPID SPECTROPHOTOMETRIC DETERMINATION OF COPPER IN NON-FERROUS ALLOYS

A very simple method has been established for the rapid determination of copper, employing the formation of the chlorocupric anion by means of concentrated hydrochloric acid. The absorption of the chlorocupric anion is measured spectrophotometrically at a wavelength of 950 mμ. The method is applicable to a wide variety of samples, including many non-ferrous alloys.

G. LINDLEY, *Anal. Chim. Acta*, 24 (1961) 161–166

THE SPECTROPHOTOMETRIC DETERMINATION OF MICROGRAM AMOUNTS OF CERIUM

A spectrophotometric procedure, which has a coefficient of variation of *ca.* 2%, is described for the determination of up to 80 μg of cerium. Ceric ion formed by oxidation with persulphate, in the presence of catalytic amounts of silver, is reduced to the cerous state by treatment with excess ferrous–phenanthroline reagent. The decrease in optical density of the ferrous–phenanthroline compared with the reagent blank is a measure of the amount of cerium present. The only common cations which cause serious interference are Mn^{+2} and Cr^{+3}.

F. CULKIN AND J. P. RILEY, *Anal. Chim. Acta*, 24 (1961) 167–170

DETERMINATION OF TARTARIC ACID WITH LEAD TETRAACETATE

(in French)

It was found, that in a medium of 80% acetic acid, in the presence of potassium acetate the oxidation of tartaric acid by lead(IV)-acetate takes place quantitatively. In the indirect determination of tartaric acid and tartrates, an excess of lead(IV)-acetate is used, allowing 30 min for the reaction to take place. The remaining reagent is then determined by potentiometric titration with a volumetric hydroquinone solution.

A. BERKA, *Anal. Chim. Acta*, 24 (1961) 171–174

METHOD FOR DETERMINATION OF THE EQUIVALENCE POINT IN POTENTIOMETRIC TITRATIONS

A method is developed for calculating the end-point and the ionization constant in a potentiometric titration. The influence of dilution is studied. The method is compared with the procedure of KOLTHOFF and that of HAHN.

J. M. H. FORTUIN, *Anal. Chim. Acta*, 24 (1961) 175–191

POLAROGRAPHIC ANALYSIS USING POTASSIUM IODIDE AS A SUPPORTING ELECTROLYTE

III. THE POLAROGRAPHIC BEHAVIOR OF TRIVALENT ARSENIC

The polarography of arsenic(III) in 0.1 or 1.0 *M* potassium iodide solutions has been studied.

T. MATSUMAE AND R. NAKASHIMA, *Anal. Chim. Acta*, 24 (1961) 192–199

CONTRIBUTIONS TO THE COMPLEXOMETRIC DETERMINATION OF CATION MIXTURES

III. SIMULTANEOUS TITRATION OF IRON(III) AND ALUMINIUM IN THE PRESENCE OF AMMONIUM THIOCYANATE AS INDICATOR

With thiocyanate as indicator iron(III) and aluminium(III) can be titrated simultaneously if $[Fe^{+3}]/[Al^{+3}] \leqq 1/4$; iron(III) is titrated directly with EDTA, and aluminium(III) is determined by back-titration of the excess of EDTA with cobalt nitrate solution in an acetone–water medium.

C. LITEANU, I. LUKÁCS AND C. STRUSIEVICI, *Anal. Chim. Acta*, 24 (1961) 200–202

CONCENTRATING TRACES OF COPPER FROM 1 *M* AMMONIUM CHLORIDE

(Short Communication)

R. TURSE AND WM. RIEMAN III, *Anal. Chim. Acta*, 24 (1961) 202–203

A RAPID AND SENSITIVE SUB-MICRO PHOSPHORUS DETERMINATION

(Short Communication)

C. J. F. BÖTTCHER, C. M. VAN GENT AND C. PRIES, *Anal. Chim. Acta*, 24 (1961) 203–204

SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 24, No. 3, March 1961

THE VOLUMETRIC ANALYSIS OF PHOSPHATES

A method has been developed for the volumetric determination of orthophosphate, and a simple variation permits the determination of the average number of phosphorus atoms per molecule in condensed phosphates. For total P_2O_5 the phosphates are converted to the diacid ortho-salt and precipitated as silver phosphate. The liberated acid is then titrated. For determination of chain length the condensed phosphate is converted to the diacid form and treated similarly, then hydrolysed and determined as orthophosphate. The ratio of the two titrations is equal to the average number of phosphorus atoms per molecule.

D. C. CULLUM AND D. B. THOMAS, *Anal. Chim. Acta*, 24 (1961) 205–213

CATALYSTS FOR CERIUM(IV) OXIDIMETRY

DETERMINATION OF PHOSPHITE, HYPOPHOSPHITE, TELLURIUM AND MERCURY

A new catalytic oxidation procedure, involving the use of a cerium(IV) sulfate reagent in perchloric acid with a mixed silver(I)–manganese(II) perchlorate catalyst, has been developed for the determination of phosphite, hypophosphite, and tellurium. By this method 15–100 mg of phosphite, 5–35 mg of hypophosphite, and 10–105 mg of tellurium may be determined with standard deviations of ± 0.17, ± 0.32, and $\pm 0.21\%$ respectively. A direct titration procedure for mercury(I) is described using a ceric perchlorate solution as titrant with the mixed catalyst system. Samples from 65–510 mg may be analyzed with a standard deviation of $\pm 0.36\%$.

G. G. GUILBAULT AND W. H. MCCURDY JR., *Anal. Chim. Acta*, 24 (1961) 214–218

A COMPLEXOMETRIC TITRATION OF INORGANIC SULPHATE IN SYNTHETIC DETERGENTS

An accurate method for the determination of inorganic sulphate in synthetic detergents has been developed. After addition of a cationic surface-active agent (cetyl pyridinium chloride) to an anionic detergent, sulphate can be determined by means of indirect titration with EDTA, using a mixture of Metalphthalein and Naphthol Green B as indicator.

H. VAN KAMP AND C. P. M. VAN DEN HONDEL, *Anal. Chim. Acta*, 24 (1961) 219–223

THERMOGRAVIMETRIC DETERMINATION OF MAGNESIUM, POTASSIUM AND LEAD BY PRECIPITATION WITH DILITURIC ACID

The thermolysis curves of magnesium, potassium, and lead dilituratе have established that either the hydrated or anhydrous forms of these precipitates are stable enough for their gravimetric use to be possible. Magnesium and lead were determined by precipitation with dilituric acid while potassium was precipitated with trimethylamine dilituratе.

A. BERLIN AND R. J. ROBINSON, *Anal. Chim. Acta*, 24 (1961) 224–234

THE IDENTIFICATION OF ALIPHATIC AMINES IN AIR AS THEIR BENZAMIDES BY PAPER CHROMATOGRAPHY

A method is described for the separation of amines as their benzamides by paper chromatography. Data are given on separations in two systems. Homologous benzamides from C_1 to C_{10} are best separated on S & S 2040a paper while C_{10} and C_{12} are separated on 2045a paper. When radiocarbon labelled benzamides were chromatographed and placed on x-ray film for eight to ten days with subsequent development of the radioautograph, the lower limit of identification was found to be *ca.* 2.5 μg of each benzamide. The results of analysis for amines in two samples of air particulate matter, and one of atmospheric vapors are presented.

J. P. LODGE JR. AND E. D. BARBER, *Anal. Chim. Acta*, 24 (1961) 235–240

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM(II) WITH 5(*p*-DIMETHYLAMINOBENZYLIDENE)RHODANINE

A sensitive spectrophotometric method has been developed for the determination of palladium, using 5(*p*-dimethylaminobenzylidene)rhodanine reagent in formic, hydrochloric, or propionic acid solution. The systems conform to Beer's law. The specific absorptivity is in the range 0.38 to 0.40 per p.p.m.–cm in the different solvents. The optimum range for 1.00-cm optical path is about 0.4 to 2.5 p.p.m. of palladium. At higher concentrations of palladium a violet-red precipitate forms within a few minutes. In propionic acid solution maximum color is attained at room temperature in 10 to 15 min, and is stable for more than two hours. The system is somewhat sensitive to hydrogen ion concentration; maximum absorbance and stability are attained at 0.01 *N* hydrochloric acid in the final solution. Platinum(IV), ruthenium(III), iridium(III), iron(III), chromium(VI), and copper(II) interfere if present in amounts several times greater than the amount of palladium; gold(III) interferes very extensively. The mole ratio method, the continuous variations method, and the slope ratio method all show the mole ratio of DMABR to palladium to be 2 : 1 in the color-forming reaction.

G. H. AYRES AND B. D. NARANG, *Anal. Chim. Acta*, 24 (1961) 241–249

IDENTIFICATION OF PHOSPHATE ANIONS IN NIOBIUM AND TANTALUM PHOSPHATES BY MEANS OF INFRA-RED SPECTRA

Some niobium and tantalum phosphates have been prepared and their infra-red spectra have been recorded and compared with those of reference substances. It has been possible to identify PO_4^{-3}, $P_2O_7^{-4}$ and possibly $P_3O_{10}^{-5}$ groups in different samples of niobium and tantalum phosphates.

S. Z. HAIDER, *Anal. Chim. Acta*, 24 (1961) 250–253

MECHANISM OF ELEMENTAL SPECTRAL EXCITATION IN FLAME PHOTOMETRY

It is generally believed that emission spectra result from thermal excitation. It is proposed that ultraviolet light present in a flame is also responsible for exciting metal atoms present. Experimentally it has been shown that the intensity of metal emission spectra is a function of the U.V. characteristics of the flame even at constant flame temperature. It was also demonstrated that spectral intensity can be enhanced by external radiation of U.V. light of the correct wavelength.

J. W. ROBINSON, *Anal. Chim. Acta*, 24 (1961) 254–262

SPECTROPHOTOMETRIC STUDY OF THE BERYLLIUM–THORIN COMPLEX AND ITS APPLICATION TO THE DETERMINATION OF BERYLLIUM IN ALLOYS

A spectrophotometric study of the beryllium complex with purified thorin shows the formation of a 1 : 1 complex at pH 12. The dissociation constant obtained after successive corrections for reagent absorbance is $1.38 \cdot 10^{-7}$. Beryllium in concentrations of 0.05% to 2.0% in copper base, zinc base, aluminium base and ferrous alloys can be determined by the formation of the thorin complex after its preliminary separation as acetylacetonate in presence of EDTA.

V. T. ATHAVALE, C. S. PADMANABHA IYER, M. M. TILLU AND G. M. VAIDYA, *Anal. Chim. Acta*, 24 (1961) 263–269

SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM WITH ASCORBIC ACID

(in German)

A method is described for the spectrophotometric determination of niobium, with ascorbic acid as reagent. A yellow colour is formed with an extinction maximum at 345 mμ.

G. E. JANAUER AND J. KORKISCH, *Anal. Chim. Acta*, 24 (1961) 270–275

APPLICATION OF THE CHRONO-AMPEROMETRY BY ANODIC REDISSOLUTION IN THE DETERMINATION OF TRACES OF TRIPHENYL TIN ACETATE

(in French)

Using a hanging dropping mercury electrode (according to VOGEL) the authors find a better sensitivity of measurements in the determination of triphenyl tin acetate as fungicide residues on vegetable matter.

P. NANGNIOT AND P. H. MARTENS, *Anal. Chim. Acta*, 24 (1961) 276–279

AMPEROMETRIC ARGENTIMETRIC AND MERCURIMETRIC TITRATION OF SULFHYDRYL

II. MERCURIMETRIC TITRATION

The ampero-mercurimetric titration of cysteine (RSH), glutathione (GSH), thioglycolic acid (TSH) and 2-mercaptoethanol (ESH) at the RMPE at pH 9 yields a sharply defined end-point corresponding to the composition $(XS)_2Hg$. Under the same conditions with the RPtWE two breaks are observed in the titration lines with RSH and GSH, corresponding to compositions $(RS)_2Hg$ and $(RS)_2Hg_2$ respectively. On the other hand, with TSH and ESH only one clear break is found at the RPtWE corresponding to $(TS)_2Hg$ or $(ES)_2Hg$. Conditions have been described for the accurate mercurimetric titration of the thiol compounds at pH 2 in the presence of 0.01 *M* sulfur dioxide at the RMPE. Use of this can be made in the determination of disulfides and in the determination of the equilibrium concentrations of the reaction between a disulfide and a sulfite at varying pH.

I. M. KOLTHOFF AND J. EISENSTÄDTER, *Anal. Chim. Acta*, 24 (1961) 280–293

SPECTROPHOTOMETRIC DETERMINATION OF ALUMINIUM WITH STILBAZO

The use of stilbazo as a spectrophotometric reagent for aluminium has been investigated. The reagent forms a stable coloured complex with aluminium showing an absorption maximum at 500 mμ. The system obeys Beer's law from 0.1–0.8 p.p.m. aluminium. The molar extinction coefficient and the stoichiometric composition of the coloured complex have been determined.

C. U. WETLESEN AND S. H. OMANG, *Anal. Chim. Acta*, 24 (1961) 294–297

SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 24, No. 4, April 1961

EXTRACTION OF BISMUTH AS IODIDE WITH ISOAMYL ACETATE AND ISOAMYL ALCOHOL

The optimum iodide concentration (excess) for the extraction of bismuth as BiI_3 into isoamyl acetate from 1–5 *N* sulfuric acid solution is approximately $5 \cdot 10^{-3}$ *M*. At this iodide concentration the extraction coefficient [Bi] isoamyl acetate/[Bi] H_2O is approximately 130 (25–30°) when the ratio of isoamyl acetate to aqueous phase is 1 : 4. Mixtures of isoamyl acetate and isoamyl alcohol in the proper ratios extract BiI_3 to a greater extent than either solvent alone.

H. A. Mottola and E. B. Sandell, *Anal. Chim. Acta*, 24 (1961) 301–306

COMPLEXOMETRIC TITRATION OF URANIUM (IV)
(*in German*)

A complexometric titration is described for the determination of uranium(IV). Solochrome Black 6BN is used as indicator. The reduction of uranium(VI) is performed with zinc in hydrochloric acid solution.

J. Korkisch, *Anal. Chim. Acta*, 24 (1961) 306–310

STUDIES OF THE SOLVENT EXTRACTION OF INDIUM OXINATE

An investigation of the extraction of radio-labelled $2 \cdot 10^{-5}$ *M* indium from various aqueous solutions into a number of organic solvents containing oxine has been carried out. The effects of pH value, oxine concentration, masking agents, different organic phases, and temperature have been studied. Extraction constants and pH values of 50% extraction have been measured and compared with theoretically-calculated values.

G. K. Schweitzer and G. R. Coe, *Anal. Chim. Acta*, 24 (1961) 311–315

THE DETERMINATION OF ANTIMONY(III) AND FREE HCl IN MIXTURES

Antimony trichloride in a boiling aqueous solution reacts quantitatively with alkali yielding the trioxide Sb_2O_3. This can be employed for alkalimetric titration of antimony trichloride. When the method is combined with the iodimetric titration of antimony(III), free hydrochloric acid can be determined in presence of the trichloride.

S. S. M. A. Khorasani, *Anal. Chim. Acta*, 24 (1961) 316–318

THERMOGRAVIMETRIC DETERMINATION OF ETHYLENEDIAMINE AND QUININE WITH DILITURIC ACID

SOLUBILITIES OF SOME POLYMETHYLENEDIAMINE DILITURATES

The thermolysis curves of ethylenediamine, trimethylenediamine, tetramethylenediamine, pentamethylenediamine, trimethylamine and quinine dilituratcs were determined. These curves established that either the hydrated or the anhydrous form of ethylenediamine and quinine dilituratc is stable enough for their gravimetric use to be possible. Both ehylenediamine and quinine were determined by precipitation with alcoholic dilituric acid solution. In addition the solubilities of some polymethylenediamine dilituratcs were determined.

A. BERLIN AND R. J. ROBINSON, *Anal. Chim. Acta*, 24 (1961) 319–328

ANALYSIS OF PERMANENT GASES BY GAS–SOLID CHROMATOGRAPHY USING AN IONISATION METHOD FOR DETECTION

A method is described for the analysis of hydrogen, oxygen, nitrogen, methane and carbon monoxide by gas–solid chromatography, using an ionisation method for detection. Accuracies of determination comparable with those of the best katharometers are attainable, without the need for the high accuracy of flow control or careful thermostatic control associated with katharometers. An ultimate detection level of 0.1 μl of s.t.p. gas can be obtained.

J. F. ELLIS AND C. W. FORREST, *Anal. Chim. Acta*, 24 (1961) 329–333

ABSORPTION OF AMINES ON CATION EXCHANGE RESINS

All the amines studied are absorbed in excess of the exchange capacity by sulfonated polystyrene resins from aqueous solutions; the absorption is greatest with benzylamine, whose molecular structure is the closest to that of the monomer of the resin. The absorption is greater, the less the crosslinking of the resin, and it is influenced by the electrostatic field of the resin cations. There is no excess absorption from solvents such as alcohols, acetic acid or dioxane. The absorption characteristics of amines are sufficiently different that separations by elution chromatography on cation exchange resins are possible. Two such separations have been demonstrated. For quantitative analytical use, however, it would be wise to use very fine mesh resins on account of the slowness of diffusion of large amine molecules within the resins.

S. R. WATKINS AND H. F. WALTON, *Anal. Chim. Acta*, 24 (1961) 334–342

GAS–LIQUID CHROMATOGRAPHIC ANALYSIS OF AROMATIC HYDROCARBONS BOILING BETWEEN 202° AND 280° IN A LOW-TEMPERATURE COAL TAR

Gas–liquid chromatography, coupled with infrared and ultraviolet spectrophotometry, was used to analyze aromatic hydrocarbons boiling between 202° and 280° in the neutral oil portion of a low-temperature bituminous coal tar. A total of 48 compounds was identified, of which 20 were alkylnaphthalenes. Of these compounds, nine had also been mentioned in a previous report. Quantitative determinations were made on nearly all of the components. The analysis, especially from a quantitative standpoint, is by far the most detailed one carried out to date for the alkylnaphthalene cut of a low-temperature coal tar. It was shown that alkylnaphthalenes with equal numbers of carbon atoms in their alkyl groups displayed a linear relationship between log relative retention and normal boiling point, a situation similar to that for the alkylbenzene series, and that the values for the C_{11}, C_{12} and C_{13} alkylnaphthalenes lie on three parallel lines. Examples of the utility of these correlations are given.

T.-C. L. CHANG AND C. KARR JR., *Anal. Chim. Acta*, 24 (1961) 343–356

CATION EXCHANGE BEHAVIOUR OF STRONTIUM ON DOWEX 50W-X8

SEPARATION FROM MIXTURES

The cation exchange chromatography of strontium on Dowex 50W-X8 is described. Nitric acid, hydrochloric acid, ammonium chloride, sodium nitrate, ammonium acetate and citric acid were examined as eluants. Strontium can be separated from important fission products such as caesium, zinc, cadmium, silver and zirconium and also from uranium(VI), thorium, bismuth, iron(III), copper(II) and mercury(II).

S. K. MAJUMDAR AND A. K. DE, *Anal. Chim. Acta*, 24 (1961) 356–359

THE COLORIMETRIC MICRO-DETERMINATION OF NICKEL AS TRIPHENYLMETHYLARSONIUM BIS-DITHIO-OXALATO NICKELATE(II)

The colorimetric micro-determination of nickel described involves the formation of $[Ph_3MeAs]_2[Ni(C_2S_2O_2)_2]$ and its extraction into an organic solvent. As the extracted compound is strongly coloured, its concentration is measured without further treatment. The procedure given is suitable within a range of 25 to 250 μg of nickel with an average error no greater than 1%. Iron, cobalt and copper interfere seriously, and a simple method is suggested for their removal.

A. J. CAMERON AND N. A. GIBSON, *Anal. Chim. Acta*, 24 (1961) 360–364

MICRO-DETERMINATION OF TRACES OF COBALT IN CEMENTS BY SPECTROPHOTOMETRY

(in French)

Description of a method for the determination of traces of cobalt in cements, by separation by means of an exchange resin followed by spectrophotometric determination with nitroso-R salt.

W. HAERDI, J. VOGEL ET D. MONNIER, *Anal. Chim. Acta*, 24 (1961) 365–370

THE DETERMINATION OF PLUTONIUM BY MASS SPECTROMETRY USING A [242]-PLUTONIUM TRACER

An isotopic dilution method is described for the determination of plutonium in samples of irradiated uranium using a ^{242}Pu tracer. An aliquot of tracer is added to the sample and the mixture treated to ensure isotopic exchange; plutonium is then separated by an ion exchange procedure and an isotopic analysis made using an M.S.5. mass spectrometer. The precision (3σ) for an aliquot containing 0.1 μg plutonium is 0.6%. A possible application of the method would be its use for control analyses of the feed solution in a chemical plant processing natural uranium fuel elements as, for example, the Windscale primary separation plant.

R. K. WEBSTER, A. A. SMALES, D. F. DANCE AND L. J. SLEE, *Anal. Chim. Acta*, 24 (1961) 371–380

POLAROGRAPHIC MAXIMA AND SOLUTION MOVEMENTS

Solution movements during the existence of polarographic maxima have been made evident by suspending carbon black in the solution. Only upward motion is observed with maxima occurring on the negative side of the electrocapillary zero. Both upward and downward motion occur with positive maxima. Examples are found in which both upward and downward motion occur during the life of a single drop. Upward motion is associated with the early life of the drop during which the rate of surface growth is greater and also with drops having a shorter life time and hence a greater growth rate. For the two ions $Fe(CN)_6^{-3}$, and Cu^{+2}, a critical ratio of concentration to growth rate exists below which upward motion prevails and above which downward motion prevails. The motions and their directions are considered due in part to the negative character of the mercury surface as it leaves the glass capillary, the time interval for the mercury surface to lose is negative orientation, and the attraction of the ions of the solution by the non-uniformly charged surface.

W. M. MacNevin and S. R. Steele, *Anal. Chim. Acta*, 24 (1961) 381–385

ETHYL DITHIOCARBAMATE AS A SUBSTITUTE FOR HYDROGEN SULPHIDE

(Short Communication)

B. N. Sen, *Anal. Chim. Acta*, 24 (1961) 386–387

PREPARATION OF HIGH SPECIFIC ACTIVITY TIN-125 RADIOTRACER

(Short Communication)

J. W. Winchester, *Anal. Chim. Acta*, 24 (1961) 388

A SYSTEM FOR THE DETERMINATION OF OXIDES OF NITROGEN

(Short Communication)

F. Vratny, *Anal. Chim. Acta*, 24 (1961) 389–390

GRAVIMETRIC DETERMINATION OF THORIUM USING SOME CARBOXYLIC ACIDS

(Short Communication)

Ch. Bheemasankara Rao, P. Umapathi and V. Venkateswarlu, *Anal. Chim. Acta*, 24 (1961) 391

SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 24, No. 5, May 1961

THE CHARACTERISATION AND DETERMINATION OF NITROGENOUS ORGANIC BASES IN MIXTURES WITH AMMONIUM REINECKATE

The reaction between nitrogenous organic bases and ammonium reineckate was studied and was found to depend on the basicity of the bases and the pH of the reaction media. An expression is given which relates the dissociation constant pK_b of a base and the pH of the reaction; when the pK_b of a base is known the pH required for the complex formation can be calculated. The conditions for the formation of reineckates of very weak bases together with the formation of mono- and di-reineckates of dibasic substances are given. The separation of bases whose pK_b values are sufficiently far apart and the determination of mixtures of mono- and dibasic substances were effected by pH adjustment of the reaction media. The isolation of strychnine from putrified human livers is also described.

L. KUM-TATT, *Anal. Chim. Acta*, 24 (1961) 397–409

OPTIMUM "COOLING TIME" TO MINIMIZE INTERFERING ACTIVITY IN NON-DESTRUCTIVE ACTIVATION ANALYSIS

In order to choose the best "cooling time" to minimize interfering γ-rays in activation analysis, the "cooling time" has been examined theoretically. There is an optimum cooling time which depends on the time of irradiation and on the half-life of nuclide formed to be determined.

M. OKADA, *Anal. Chim. Acta*, 24 (1961) 410–412

THE COMPOSITION OF RHODAMINE B CHLOROGALLATE

The formula of rhodamine B chlorogallate has been shown to be $(RH)GaCl_4$ where R = rhodamine B.

F. CULKIN AND J. P. RILEY, *Anal. Chim. Acta*, 24 (1961) 413–414

VOLUMETRIC DETERMINATION OF PERSULPHATE IN SULPHURIC SOLUTIONS BY PERMANGANATE

The determination of persulphate in a *ca.* 12.5 *N* sulphuric acid solution by direct titration with permanganate is described. The results are satisfactory but the conditions are critical.

Y. K. GUPTA, *Anal. Chim. Acta*, 24 (1961) 415–418

IODIMETRIC DETERMINATION OF CARBON DISULPHIDE

STUDY OF THE EFFECT OF pH

The effects of pH and time on the error (due to decomposition of xanthate) involved in the iodimetric determination of carbon disulphide have been studied. A pH range of 5.4 to 5.8 (acetate-buffered) is recommended. Carbon disulphide varying in amount from 0.0060 to 0.3240 g can be determined with an error of $\pm 1.0\%$.

M. EUSUF AND M. H. KHUNDKAR, *Anal. Chim. Acta*, 24 (1961) 419–423

COMPLEXOMETRIC DETERMINATION OF CHLORIDES, CHLORATES AND PERCHLORATES IN PRESENCE OF EACH OTHER

(in French)

A method is described for the analysis of a mixture of chlorides, chlorates and perchlorates by complexometric titration. It is based on the partial reduction of chlorates and the reduction of chlorates plus perchlorates respectively; the chloride formed can then be determined.

A. DE SOUSA, *Anal. Chim. Acta*, 24 (1961) 424–426

THERMOGRAVIMETRIC CHARACTERISTICS OF BARBITURIC ACID AND SOME OF ITS DERIVATIVES

The thermolysis curves of barbituric acid and some of its derivatives have been determined. Barbituric acid, violuric acid and dilituric acid form hydrates while 1,3-dimethylvioluric acid and barbital are anhydrous. Barbital and 1,3-dimethylvioluric acid sublime before decomposition. The differential thermal analysis for dilituric acid showed a sharp exotherm at 190° indicating a violent explosion.

A. BERLIN, M. E. TAYLOR AND R. J. ROBINSON, *Anal. Chim. Acta*, 24 (1961) 427–431

THERMOGRAVIMETRIC AND MAGNETIC CHARACTERISTICS OF SOME INORGANIC SALTS OF DILITURIC ACID

The thermolysis curves of the transition metal dilituratesas well as those of copper, zinc, cadmium, ammonium and rubidium have been determined. These dilituratewith the exception of ammonium and rubidium dilituratesform hydrates. The oxides of the corresponding metals are obtained at relatively low temperatures. Magnetic susceptibility measurements show that these compounds are "essentially ionic" salts.

A. BERLIN AND R. J. ROBINSON, *Anal. Chim. Acta*, 24 (1961) 432–437

OBSERVATIONS ON THE USE OF AN ANION EXCHANGE RESIN IN THE DETERMINATION OF AMINOBENZOIC ACIDS, AMINOPHENOLS AND SOME RELATED SUBSTANCES IN BIOLOGICAL MATERIALS

An anion exchange resin (Dowex 1X10) has been studied for the purpose of separating aminobenzoic acids, aminophenols, sulphanilamide and nicotinic acid, preparatory to their determination by colorimetric methods.

S. L. TOMPSETT, *Anal. Chim. Acta*, 24 (1961) 438–443

CHROMATOGRAPHIC SEPARATION OF IONS IN PRESENCE OF OXALATE, TARTRATE AND CITRATE, WITH AQUEOUS ETHANOL AS SOLVENT. I

The paper chromatographic separation of Ag, Hg, Pb, Bi, Cu, Cd, Co, As(III), Sb(III) and Sn(II) in mixtures of 3, 4 or 5 of these ions has been studied in the absence and presence of oxalate, citrate and tartrate with aqueous ethanol as solvent.

E. J. SINGH AND A. K. DEY, *Anal. Chim. Acta*, 24 (1961) 444–445

QUANTITATIVE CHROMATOGRAPHIC ANALYSIS USING RECTIFIED RADIO-FREQUENCY METHODS. I. LITHIUM, SODIUM AND POTASSIUM

The BLAKE Zone Detector has been shown to be a very useful apparatus for the location of ion zones separated by paper chromatography. In the case of the alkali metals, these zones can be estimated by measuring the impedance of their aqueous extract. An alternative method, that of measuring the area under the detector curve, does not provide a practical means of quantitative measurement. A new developing solvent is described for the paper chromatographic separation of lithium, sodium and potassium chlorides.

J. A. BROOMHEAD AND N. A. GIBSON, *Anal. Chim. Acta*, 24 (1961) 446–450

DETERMINATION OF LEAD IN GASOLINE BY ATOMIC ABSORPTION SPECTROSCOPY

A procedure has been developed for the direct determination of lead in gasoline by atomic absorption spectroscopy. This procedure is rapid, does not require expensive equipment, is remarkably free from interference by other trace elements present, and allows considerable variation in the sulfur and nitrogen content of the gasoline. It compares favorably with other existing procedures for this determination, such as X-ray fluorescence, wet chemical methods, and flame photometry.

J. W. ROBINSON, *Anal. Chim. Acta*, 24 (1961) 451–455

THE DETERMINATION OF INDIUM AND THALLIUM IN SILICATE ROCKS BY A COMBINED SOLVENT EXTRACTION AND SPECTROCHEMICAL TECHNIQUE

A technique has been developed for the determination of In and Tl at very low concentrations in silicate rocks. The iodo-complexes of these elements are extracted from the rock silicate into ethyl ether and the ethereal residues are analysed spectrochemically. The optimum working conditions were established by a study of the variation of percentage extraction as a function of hydrogen iodide normality; the reproducibility of the spectrochemical procedure was investigated. In and Tl were determined in eight silicate rocks including standard granite G-1 and standard diabase W-1. Good agreement was obtained with results of other workers for these two rocks and with the author's previous results. The evidence for a In/Mn coherence in silicate rocks is sufficiently strong to warrant further investigations.

R. R. BROOKS, *Anal. Chim. Acta*, 24 (1961) 456–462

CONTRIBUTIONS TO THE STUDY OF ORGANIC OSMIUM REAGENTS

The reaction of osmium is examined with two thiourea derivatives and four heterocyclic nitrogen compounds containing the SH-group attached to the ring, and five new colorimetric methods for the determination of osmium in the range 1.04–41.44 μg Os/ml are proposed.

GH. BAIULESCU, C. LAZĂR AND C. CRISTESCU, *Anal. Chim. Acta*, 24 (1961) 463–466

THIONIN DERIVATIVES IN THE EXTRACTION AND DIRECT PHOTOMETRIC DETERMINATION OF BORON

Thionin and nine commercially available thionin derivatives were studied for their applicability in the analytical solvent extraction and direct photometric determination of boron. Azure A, Azure B, Azure C, Methylene Blue, New Methylene Blue N, Methylene Green, Toluidine Blue O, Thionin and the eosinates of Azure A and B were investigated. Over thirty organic solvents, mostly chlorinated or brominated were tried with these dyes. 1,2-Dichloroethane, 1,2-dichloropropane, dichloromethane, 1,1,2-triochloroethane, *cis*-dichloroethylene, *o*-dichlorobenzene, 1,4-dichlorobutane and mixtures of these solvents proved applicable. Many good dye–solvent combinations were found which were very attractive for the separation and determination of various amounts of boron. Only thionin itself proved unsatisfactory.

L. PÁSZTOR AND J. D. BODE, *Anal. Chim. Acta*, 24 (1961) 467–473

DETERMINATION OF SULPHANILAMIDES WITH ALKYL NITRITES BY A POTENTIOMETRIC METHOD

A potentiometric titration with alkyl nitrite solutions is described for the determination of various sulpha drugs.

N. K. MATHUR, S. P. RAO AND O. P. KACHHAWAHA, *Anal. Chim. Acta*, 24 (1961) 474–475

OSCILLOPOLAROGRAPHIC DETECTION AND DETERMINATION OF IODATE AND PERIODATE

(in German)

The oscillopolarographic behaviour of periodate and iodate has been investigated in acid, neutral and alkaline electrolytes. The detection and determination of periodate in iodate may be carried out using iodate as electrolyte and the detection and determination of iodate in periodate may be carried out using 5 *M* sodium hydroxide as electrolyte.

A. BERKA AND J. DOLEŽAL, *Anal. Chim. Acta*, 24 (1961) 476–480

THE USE OF MICROCHEMICAL METHODS IN RADIOCHEMICAL ANALYSIS

Techniques used at A.W.R.E. during the past 6 years for the radiochemical analysis of mixtures of active nuclides using 0.5- to 1-mg quantities of carrier are described and their advantages discussed. Micro-methods are listed for chemical yield determinations by spectrophotometry and micro-titration, and details are given for the micro-titration of a number of elements with EDTA using a spectrophotometric end-point. A special fitment is described to enable the Unicam SP 600 spectrophotometer to be used for micro-titrations. Some values are given for the coefficients of variation obtained in typical chemical yield methods and in overall radiochemical deter minations of ^{99}Mo, ^{111}Ag, ^{115}Cd and ^{140}Ba.

R. G. MONK AND J. HERRINGTON, *Anal. Chim. Acta*, 24 (1961) 481–492

DETERMINATION OF TUNGSTEN IN PRESENCE OF VANADIUM

(Short Communication; in French)

A. CLAEYS, *Anal. Chim. Acta*, 24 (1961) 493

SPOT TEST FOR BENZYLAMINE AND *p*-NITROBENZALDEHYDE

(Short Communication)

F. FEIGL AND V. ANGER, *Anal. Chim. Acta*, 24 (1961) 494–495

OBSERVATIONS ON THE THERMAL DECOMPOSITION OF CUPRIC ACETATE MONOHYDRATE

(Short Communication)

J. A. HILL, C. B. MURPHY AND G. P. SCHACHER, *Anal. Chim. Acta*, 24 (1961) 496–497

SEPARATION OF NIOBIUM AND TANTALUM BY N-BENZOYL-N-PHENYLHYDROXYLAMINE

(Short Communication)

A. K. MAJUMDAR AND B. K. PAL, *Anal. Chim. Acta*, 24 (1961) 497–498

VOLTAMMETRIC DETERMINATION OF ANTIOXIDANTS AT THE WAX-IMPREGNATED GRAPHITE ELECTRODE

(Short Communication)

E. BARENDRECHT, *Anal. Chim. Acta*, 24 (1961) 498–499

SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 24, No. 6, June 1961

DETECTION OF SELENIUM IN ORGANIC SPOT TEST ANALYSIS

A test is described for the detection of selenium in organic compounds. It is based on the oxidative decomposition with hot concentrated perchloric acid to yield selenic acid, which reacts with hydrazine to give red elemental selenium. Microchemical limits of identification are reached within the technique of spot test analysis.

F. FEIGL, *Anal. Chim. Acta*, 24 (1961) 501–504

DETERMINATION OF AMINES AND ALKYL PHOSPHATES IN KEROSENE SOLUTIONS CONTAINING URANIUM AND SULPHURIC ACID

Methods for the determination of amines, alkyl phosphoric acids and tributyl phosphate in kerosene solutions containing uranium and sulphuric acid are described. Amine and alkyl phosphoric acid are determined volumetrically, after removal of interferences, by titration in chloroform solution with a dioxan solution of perchloric acid. Tributyl phosphate is determined by difference between the total phosphorus and the phosphorus from the acid alkyl phosphoric acid.

A. W. ASHBROOK, *Anal. Chim. Acta*, 24 (1961) 504–508

SOME POSSIBLE APPLICATIONS OF MASS SPECTROMETRY TO ACCOUNTING PROBLEMS IN CHEMICAL PROCESSING PLANTS

A procedure is described for the determination of the [total Pu]/[total U] concentration ratio for a given solution by an isotopic dilution method. Results obtained for two samples give a mean precision (1σ) of 0.3% for a determination made by a single mass spectrometric analysis. A possible application of the method would be its use for plutonium accounting analyses in a chemical plant processing natural uranium fuel elements, an important feature being the near elimination of the effect of plant sampling errors. An outline is also given of a similar procedure which might be used for the determination of ^{235}U in a plant processing enriched uranium–aluminium alloy reactor fuel.

R. K. WEBSTER, D. F. DANCE AND L. J. SLEE, *Anal. Chim. Acta*, 24 (1961) 509–525

RADIOCHEMICAL SEPARATION OF COBALT

A method is described for the radiochemical separation of cobalt based on the extraordinary stability of cobalt diethyldithiocarbamate. Interferences are few; only very small amounts of zinc and iron accompany cobalt, which is important in neutron-activation analysis.

P. C. VAN ERKELENS, *Anal. Chim. Acta*, 24 (1961) 526–528

SOME REMARKS ABOUT THE USE OF THE BOMB CALORIMETER

In order to reduce the unfavourable influence of unknown thermometer errors, the method for the determination of the calorific value of organic matter in the calorimetric bomb is modified so that in all determinations nearly the same section of the thermometer is used. For the correction of the observed temperature rise a very simple formula is derived from the more elaborate formula of REGNAULT–PFAUNDLER.

H. J. NIJKAMP, *Anal. Chim. Acta*, 24 (1961) 529–532

DETERMINATION OF FORMIC ACID BY CATALYTIC OXIDATION WITH CERIUM(IV)

A method is proposed for the determination of formic acid by oxidation with cerium(IV) in presence of potassium bromide. The method can also be used for the further oxidation of organic compounds which yield formic acid under ordinary conditions with cerium(IV).

N. K. MATHUR, S. P. RAO AND D. R. CHOWDHARY, *Anal. Chim. Acta*, 24 (1961) 533–535

A NEW RAPID SEMIMICRO TITRIMETRIC DETERMINATION OF MERCURY

Mercury(II) (0.5 to 5 mg) can be determined accurately by titration with potassium iodide solution in presence of potassium periodate and carbon tetrachloride as indicator. The simple and rapid method is applicable to many mercurial compounds and preparations; interferences are few.

K. C. SEAL, *Anal. Chim. Acta*, 24 (1961) 536–540

HYDRAZINE AS A TITRIMETRIC REAGENT IN IODOMETRY. I

The preparation, standardisation and stability of hydrazine solution is described. The optimum conditions for the titration with hydrazine solution of pure iodine solution of iodine liberated from oxidants and of excess of iodine left after oxidation of certain reductants have been determined. The advantages of hydrazine over other iodometric reagents are discussed.

K. S. PANWAR, N. K. MATHUR AND S. P. RAO, *Anal. Chim. Acta*, 24 (1961) 541–545

REDOX INDICATORS IN INDIRECT TITRATIONS OF ANIONS

DETERMINATION OF PHOSPHATE IONS BY MEANS OF LEAD NITRATE

An indirect titration of phosphate with lead(II) nitrate solution is proposed; excess of lead is titrated with potassium ferrocyanide in presence of variamine blue as redox indicator.

Z. GREGOROWICZ, D. MAZOŃSKA AND D. PRAJSNAR, *Anal. Chim. Acta*, 24 (1961) 546–547

CHELATES OF 4-HYDROXYBENZOTHIAZOLE WITH THE RARE EARTHS

The rare earth chelates of 4-hydroxybenzothiazole have been prepared and analyzed by a titrimetric method as well as a microgravimetric method. The infrared spectra of these chelates have been determined.

P.-K. FENG AND Q. FERNANDO, *Anal. Chim. Acta*, 24 (1961) 548–554

COLORIMETRIC MICRODETERMINATION OF BORON IN AQUEOUS MEDIA, WITH REAGENTS CONTAINING AZO OR IMINE GROUPS, DERIVATIVES OF THE ACIDS H AND K

(in French)

For the colorimetric microdetermination of boron, 19 dye-stuffs containing imine or azo groups have been examined; only 6 of these were usable and much the best was azomethine-H. This reagent can be used in aqueous media.

R. CAPELLE, *Anal. Chim. Acta*, 24 (1961) 555–572

FLAME-PHOTOMETRIC DETERMINATION OF LITHIUM IN SILICATE MINERALS (ZINNWALDITCONCENTRATES)

(in German)

The flame-photometric determination of lithium in Zinnwaldit-concentrates was carried out after removal of the interfering elements (Fe, Al, Mn, Ca, K, Na, etc.) either by means of cation and anion-exchange resins or by means of CdO or basic lead carbonate. Flame photometry alone resulted in up to 8% too high lithium values.

J. LIEBIG AND H. BREDEHORST, *Anal. Chim. Acta*, 24 (1961) 573–575

THE REACTION OF SCHOENBERG'S REAGENT WITH ELEMENTAL SULFUR

The infrared absorption spectrum of SCHOENBERG's reagent, $(CH_3OC_6H_5)_2C=NCH_2C_6H_5$ has been obtained in the 650–5000 cm^{-1} region. Assignments have been made for all observed bands using group frequency methods.

W. C. NEELY AND H. B. WILLIAMS, *Anal. Chim. Acta*, 24 (1961) 575–578

ON THE USE OF BIS-CYCLOHEXANONE-OXALYLDIHYDRAZONE AND BIS-ACETALDEHYDE-OXALYLDIHYDRAZONE IN THE ANALYSIS OF COPPER

The reagents bis-cyclohexanone-oxalyldihydrazone (reagent 1) and bis-acetaldehyde-oxalyldihydrazone (reagent 2) and their complexes with copper were examined by spectrophotometry and polarography. The investigations indicated that in solution reagent 1 existed in three tautomeric forms depending of the pH of the solvent. The decomposition of these forms was studied and decomposition schemes are suggested. In the pH range employed for spectrophotometric determination of copper (7–10), solutions of reagent 1 and the copper(II)–reagent 1 complex were found to be very unstable owing to the decomposition of the ligand. Solutions of reagent 2 and its complexes with copper were found to be much more stable. The investigations further indicated that both reagents form copper(II) complexes with ligand–metal ratios 2:1. In addition a colourless copper(I)–reagent 2 complex with two ligands was found polarographically. The existence of a similar complex between copper(I) and reagent 1 is probable.

E. JACOBSEN, F. J. LANGMYHR AND A. R. SELMER-OLSEN, *Anal. Chim. Acta*, 24 (1961) 579-588

DETERMINATION OF STABILITY CONSTANTS

(Short communication)

G. CURTHOYS AND D. A. J. SWINKELS, *Anal. Chim. Acta* 24 (1961) 589

ELIMINATION OF ALUMINIUM INTERFERENCE IN COLORIMETRIC DETERMINATION OF FLUORIDE IN WATER

(Short communication)

M. C. MOREIRA DE ALMEIDA AND C. PULIDO, *Anal. Chim. Acta*, 24 (1961) 590